# Below the grain size of most materials

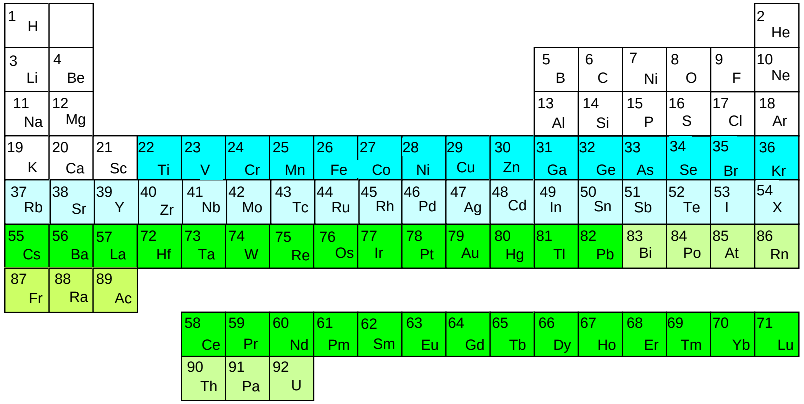
Gene E. Ice

*Oak Ridge National Laboratory*

How X-ray Microscopy in the 21st Century Will Revolutionize Our Understanding of Materials.

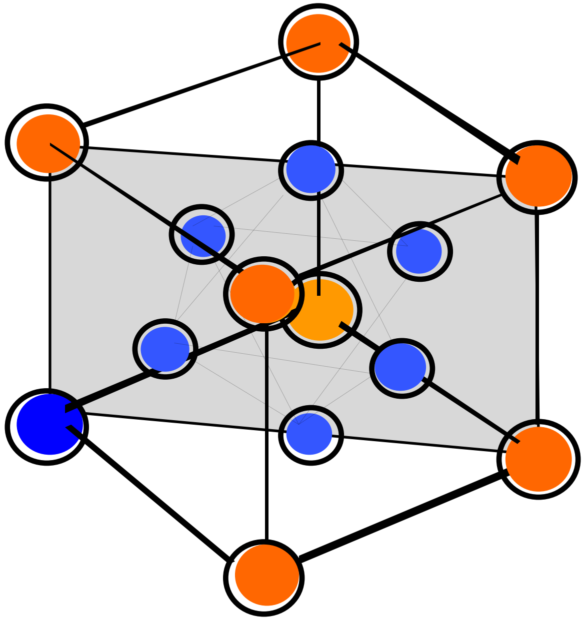
# Materials characterization begins with 3 questions

- What is the elemental composition?




- What is the crystal/local structure?

- What are the defects?

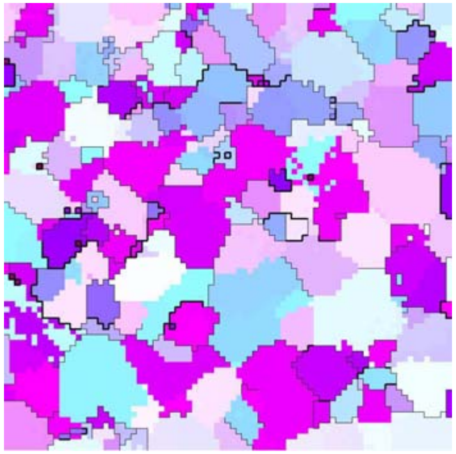


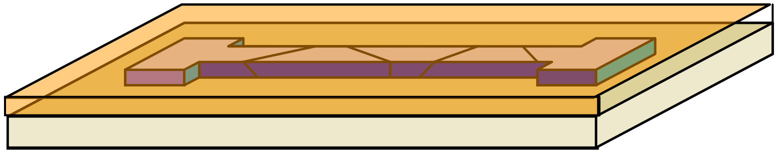
# Heterogeneity makes microbeams essential for *real* materials

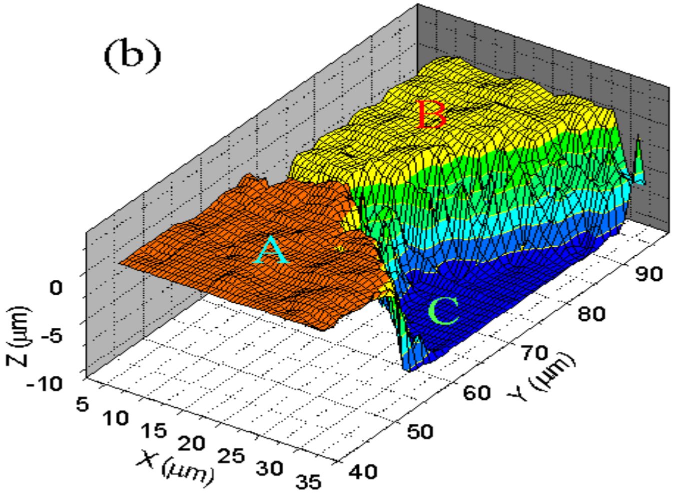
- Most materials ***polycrystalline***(0.1-50 μm)
  - Anisotropic mechanical/chemical properties

- Even ***perfect crystal*** materials have polycrystal/ heterogeneous issues
  - Strain
  - Thin films/ interconnects etc.
  - Defects

- Correlations/ distributions count!

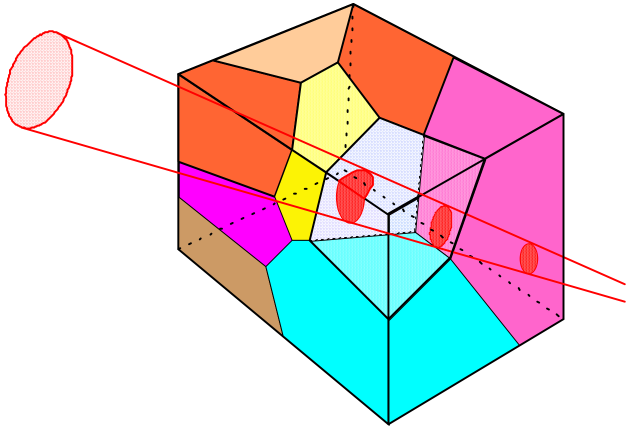




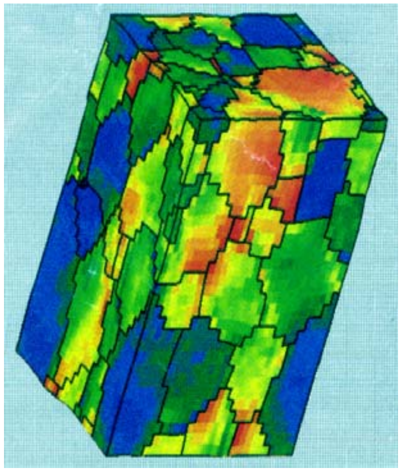


# Intense x-ray microbeams allow unprecedented measurements

- Point-to-point correlations to clarify role of heterogeneity
  - Nondestructive grain boundary mapping
  - Strain/stress distributions
  - Chemical/bonding distributions



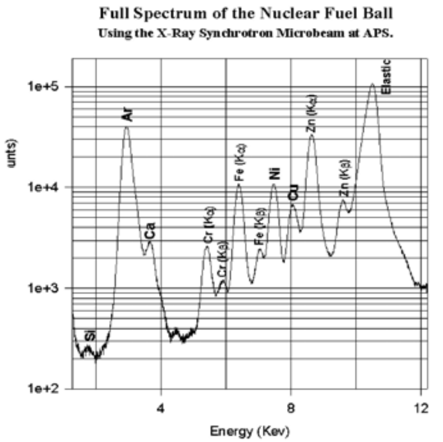
- Advanced single-crystal methods -defect characterization grains/subgrains
  - Standing wave
  - Truncation rod
  - Diffuse x-ray scattering

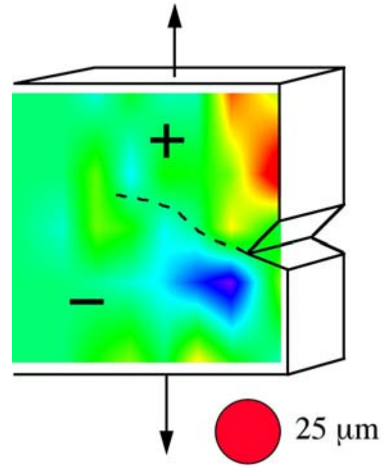


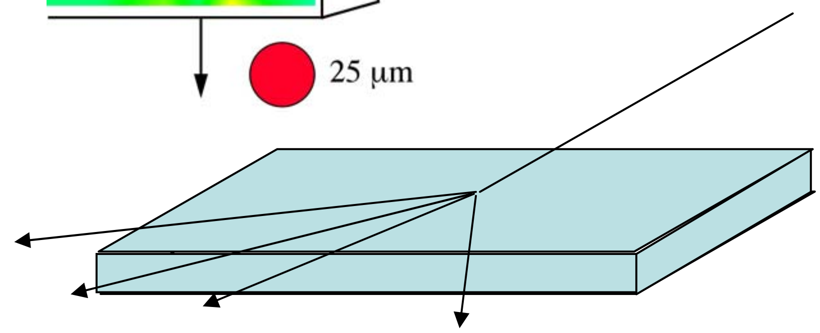
- Combinatorial analysis of materials

# Example applications have emerged over last two decades

- Microfluorescence chemical/chemistry inhomogeneity (20 years)
- Local crystal structure/strain mapping (15 years)
- Submicron surface characterization (10 years)
- Diffuse x-ray scattering from heterogeneous sample volumes (5 years)



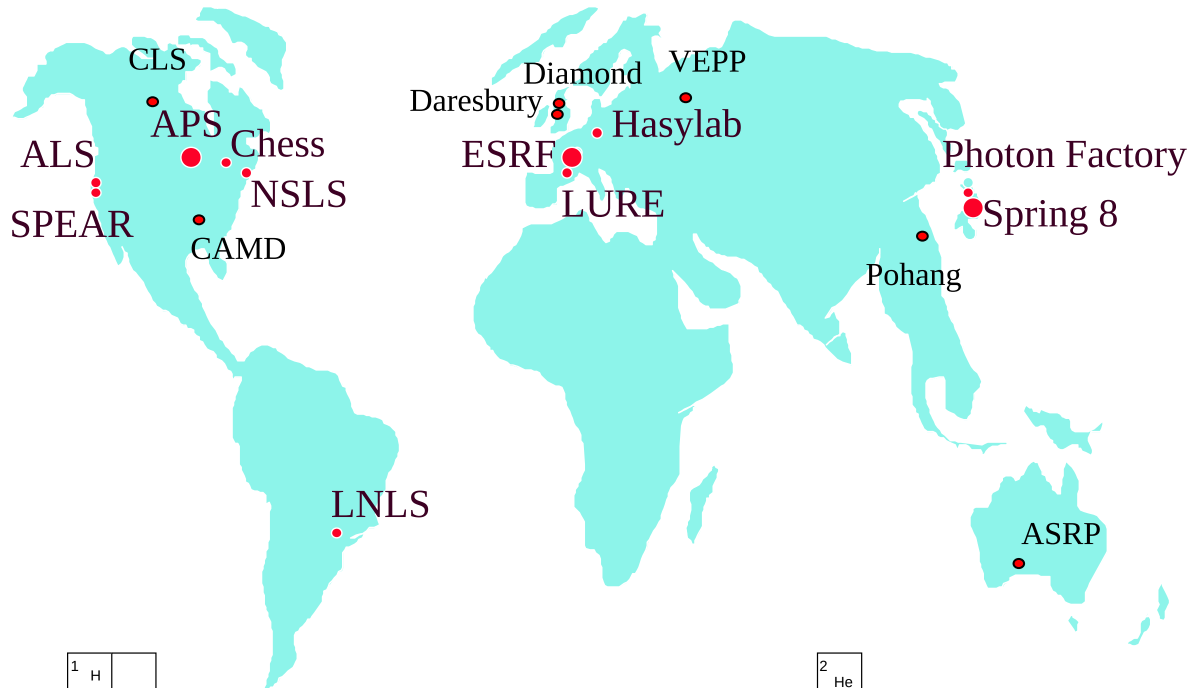



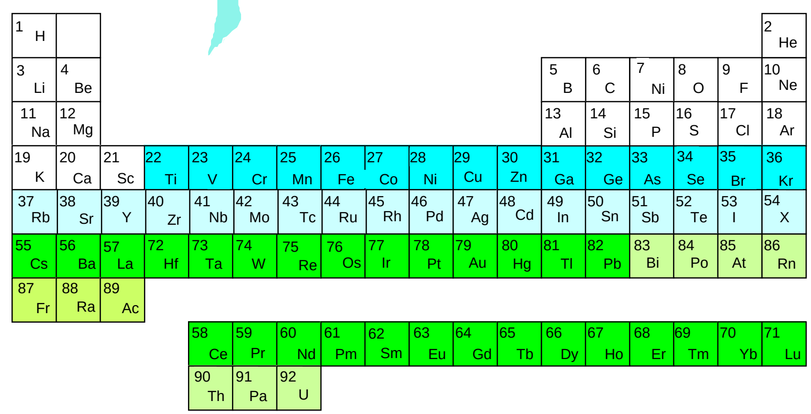
Virtually any single-crystal characterization tools can be applied to real materials!

# Microfluorescence most widely applied synchrotron microbeam technique

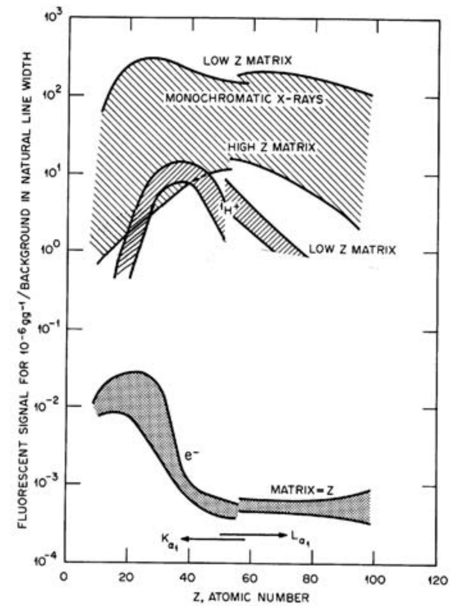
- Virtually all operating/planned sources include

- Potential for materials science still ***largely untapped***!

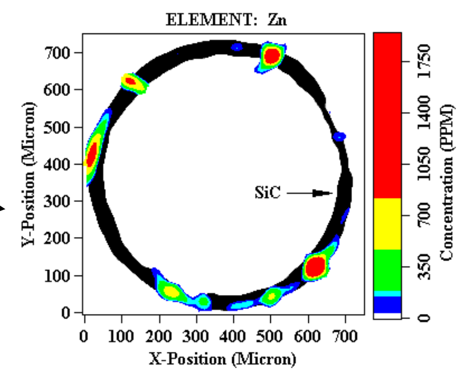


# Microfluorescence provides unprecedented nondestructive elemental distributions

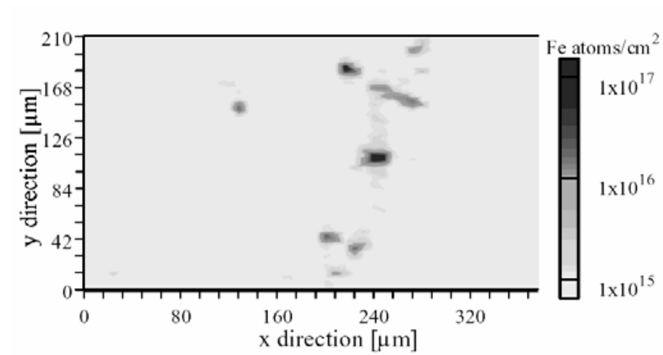



- Trace element detection
  - PPB in low Z

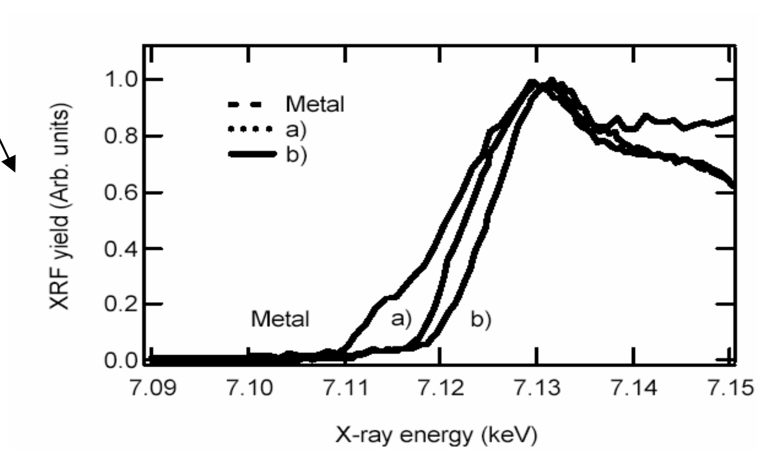



- 3D spatial distributions

- Ultra-sensitive near-surface

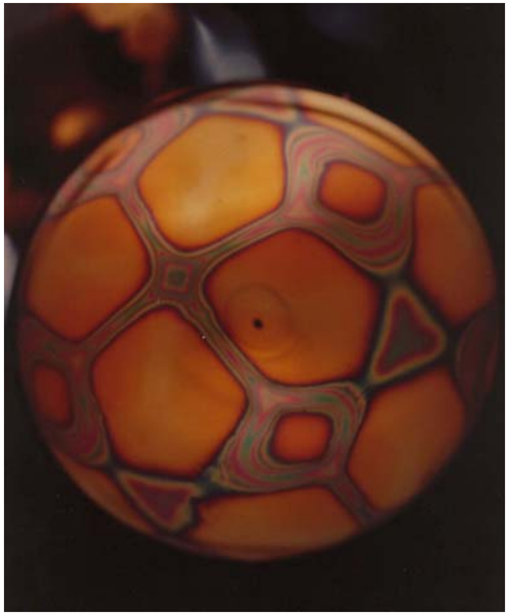


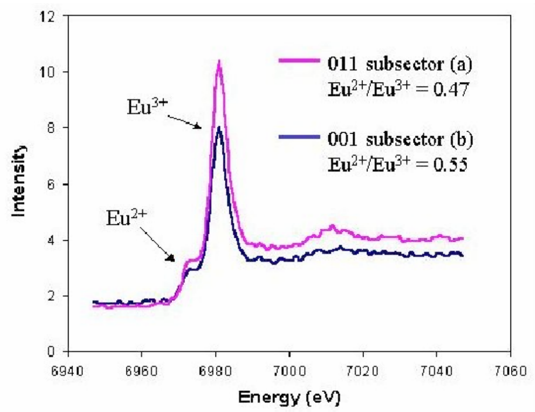

- Chemical state (μXANES)



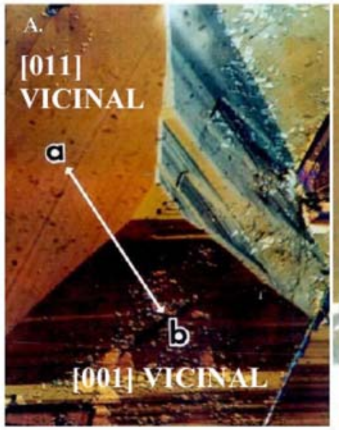
# Spatially-resolved bonding characterization underutilized materials application

- Micro XAFS/XANES widely applied biology and environmental sciences
- Huge potential in materials science

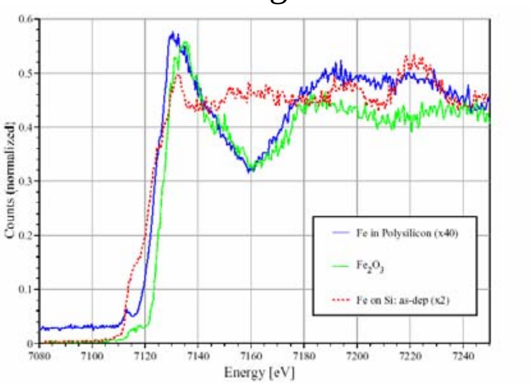





Rakovan et al.
APS Sector 13ID

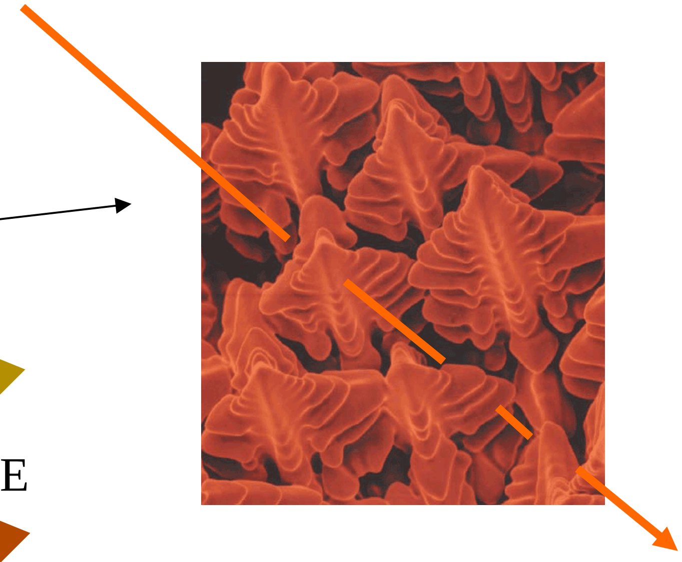



McHugo et al. ALS

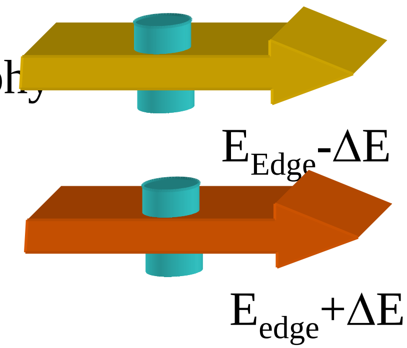



Si single crystal

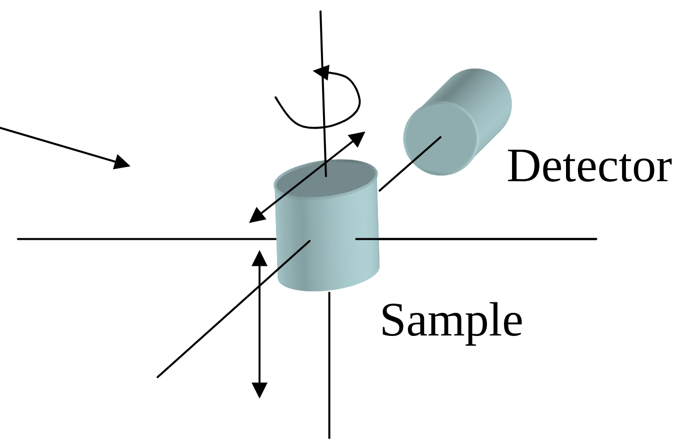
# Materials impact will increase with 3D trace-element imaging.



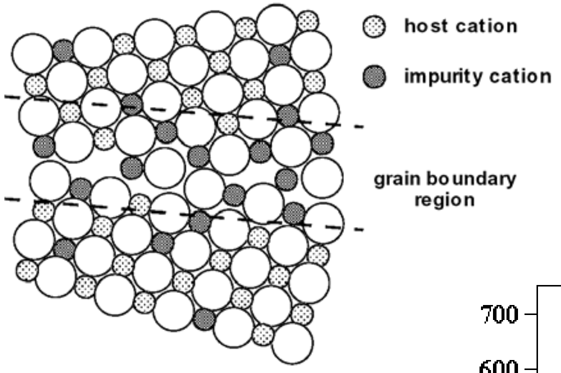
- 2D fluorescence probes blur complex 3D patterns
- Differential absorption tomography
  - Low signal-to-noise



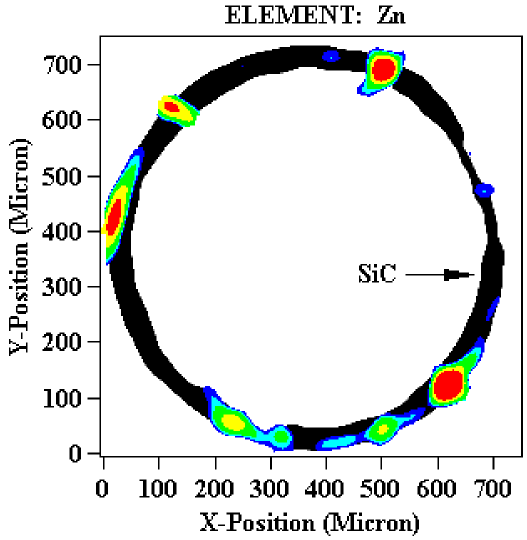

- Fluorescence microtomography
  - Pencil beam technique
- Differential aperture microscopy
  - *Requires energy sensitive area detector*

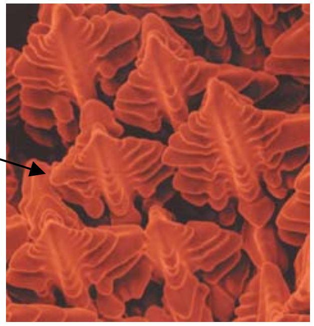


# 3D fluorescence microtomography has important materials applications




- Grain-boundary segregation
- Trace-element diffusion/contamination
- Elemental inhomogeneity during solidification

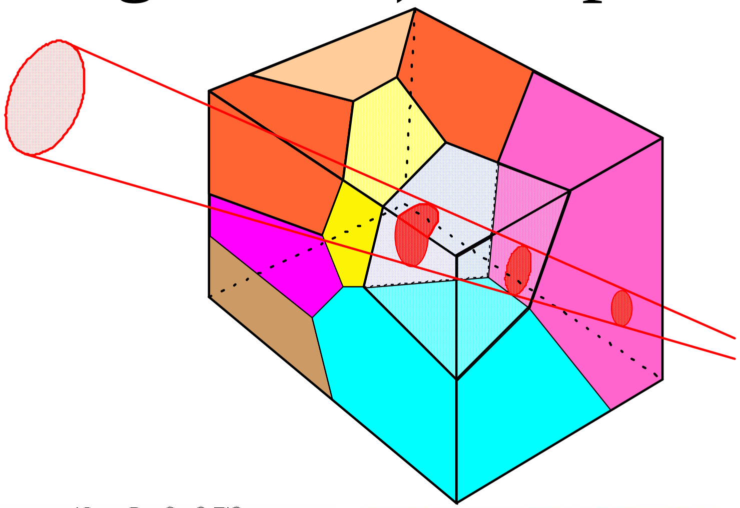


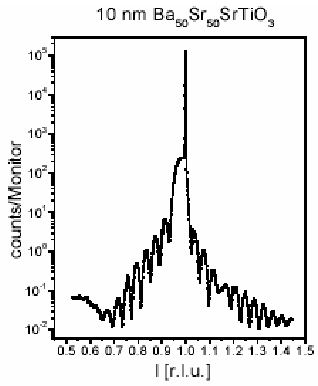
Important 2D applications remain and illustrate promise

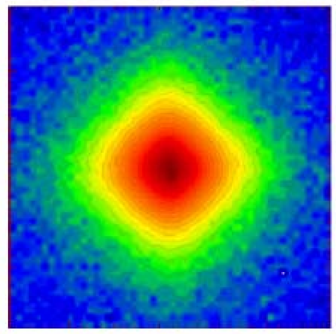
# Microbeams extend powerful single-crystal techniques to small (inhomogeneous) samples

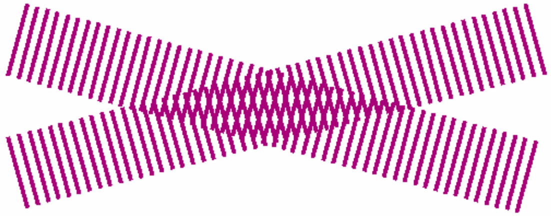
- Complex polycrystals locally dominated by single crystals, bicrystal and tri-crystal boundaries.



- Advanced interface characterization methods can be applied locally
  - Truncation rod
  - Standing wave

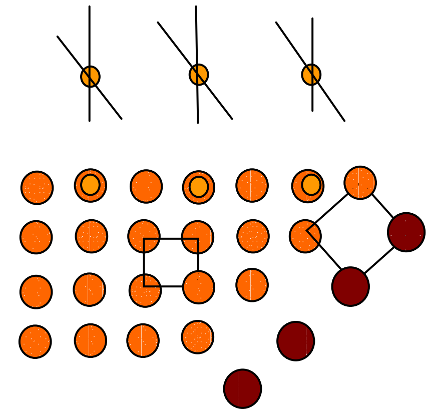


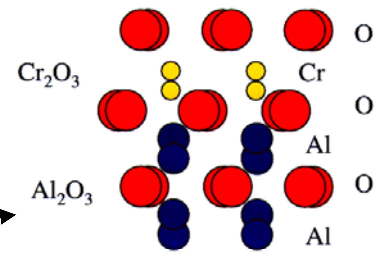





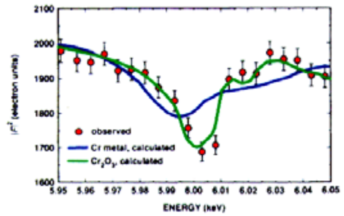
# Microbeams extend truncation rod measurements to most polycrystal samples

- Local roughness of polycrystalline grain/phase boundary interfaces/surfaces

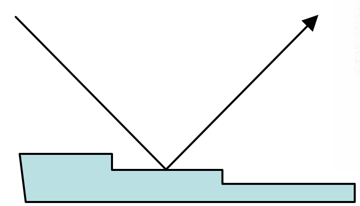


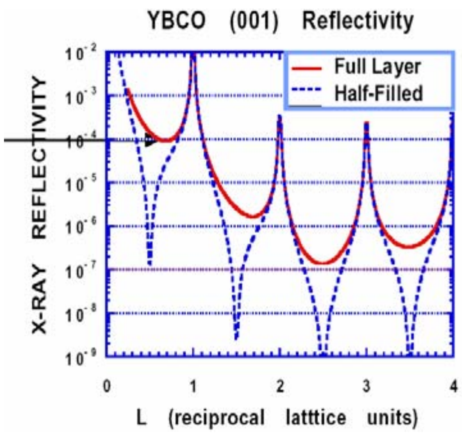



- DAFS at interfaces




- Larson proposes truncation rod from single terraces.

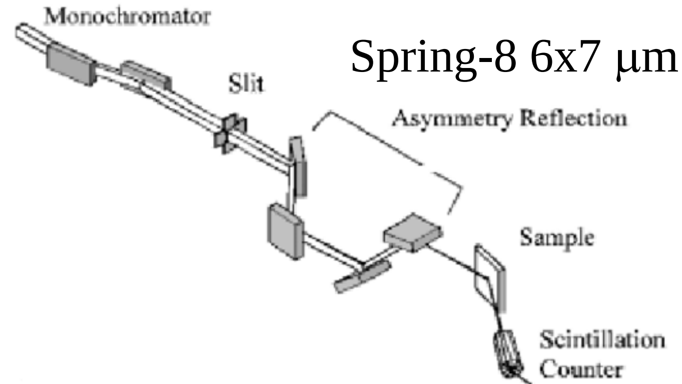




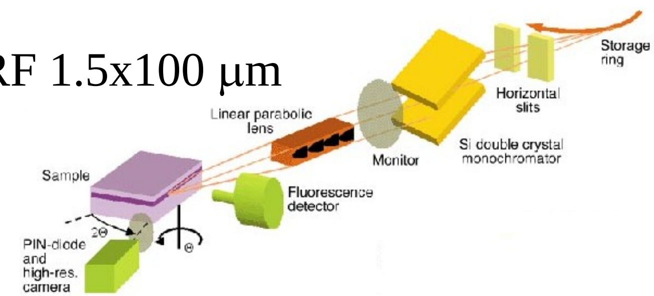
# Standing wave x-ray microprobe allows precision measurements of atom positions in imbedded layers

- Atomic resolution for atom positions near single crystals
- Precision measurements can be used to determine local strain

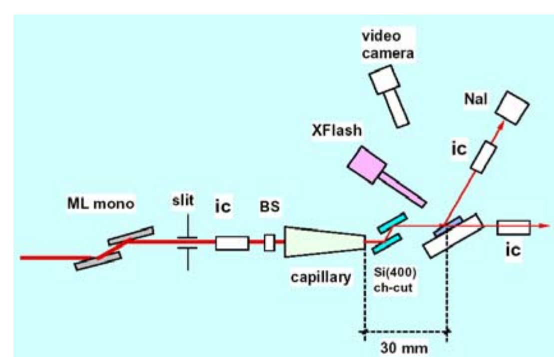
Spring-8 6x7 μm

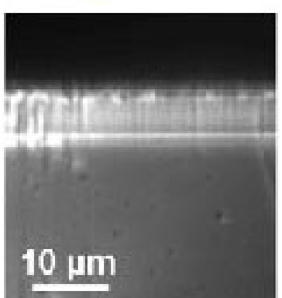


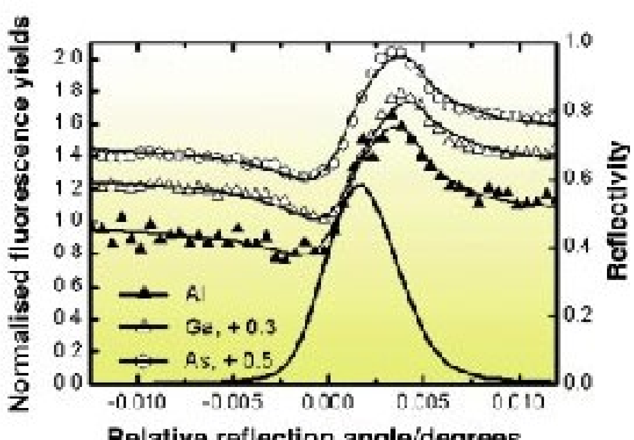

ESRF 1.5x100 μm




CHESS <1 μm



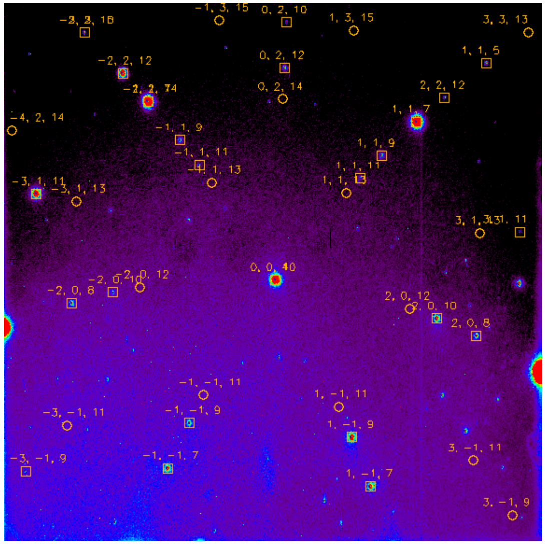



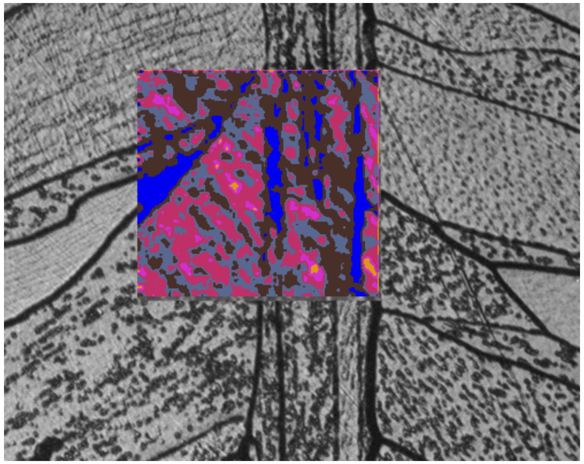
# Tremendous excitement in microdiffraction

- Unprecedented spatially resolved characterization of crystal structure
  - Phase (crystal structure)
  - Texture (local orientation)
  - Strain (elastic + plastic)

- Crystal defects
  - Dislocation types
  - Grain/phase boundary type



MicroLaue Pattern from Ni



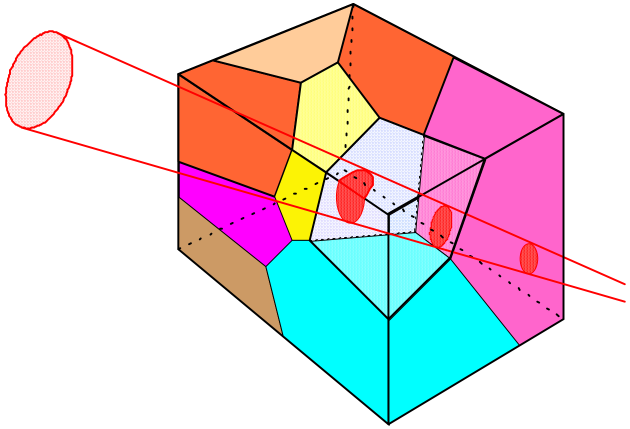
Dislocation density (Ir Weld)

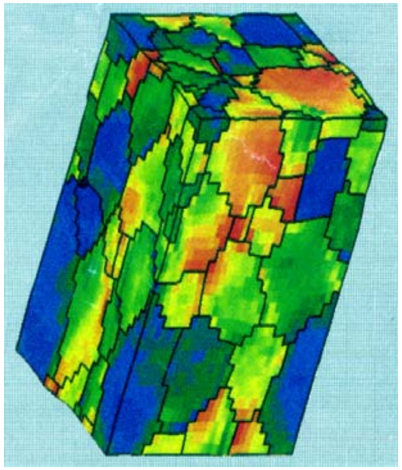
# Microdiffraction -Address Fundamental/ Long-standing Issues of Mesoscale Physics

- **3D Organization of polycrystalline materials**
  - **Colony structure-fractal behavior**
  - **Grain boundary habit/ coincident site lattice**
  - **Percolation model**

- **3D Dynamics versus local environment**
  - **Local growth, ripening**
  - **Nucleation sites- deformation energy/stress**
  - **Rotations vs. global/local environments**
  - **Orientation pinning**
  - **Curvature**

- **Fundamental assumptions**
  - **Intra- and inter-granular stresses**
  - **Grain boundary shear vs. habit**

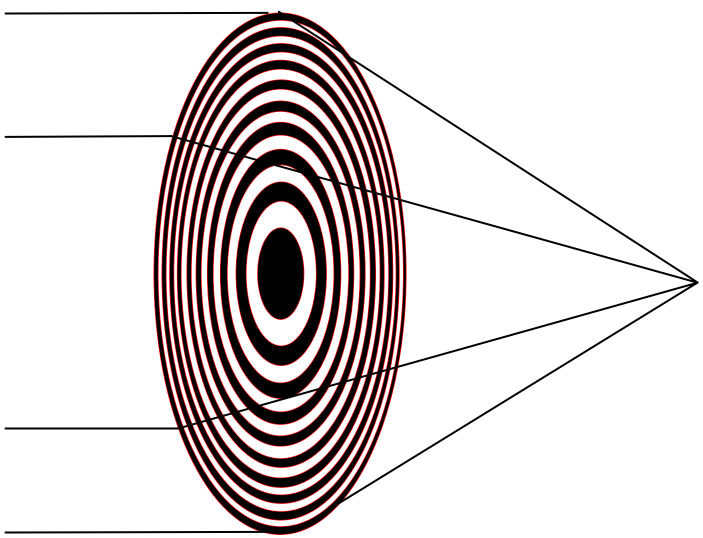


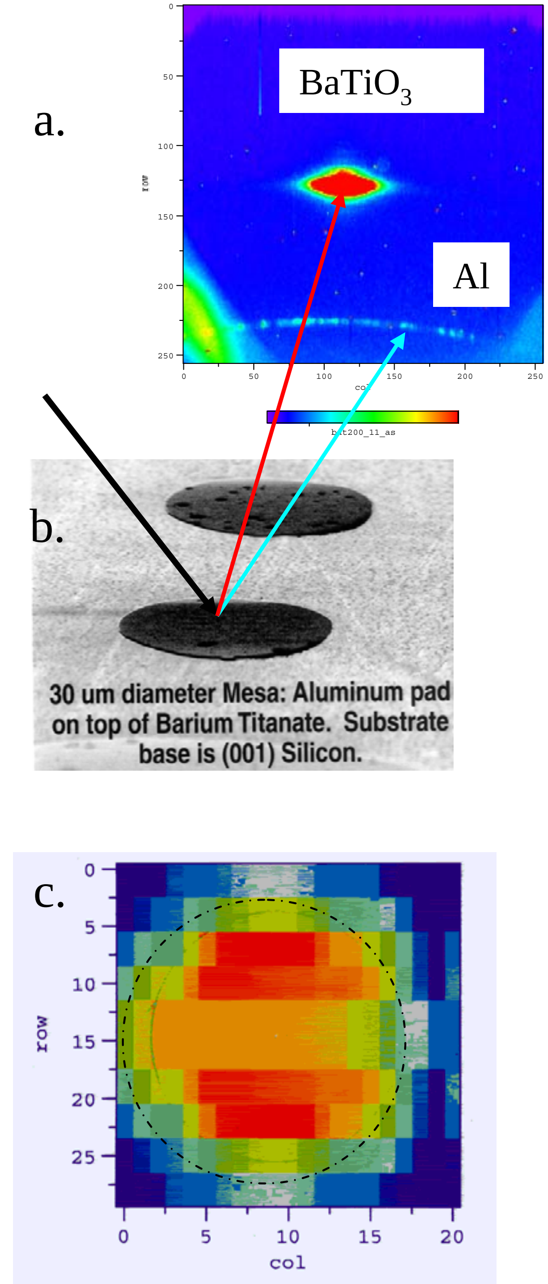


Theoretical shear stress in Deformed Cu
Holm and Battaile, **JOM** Sept. 2001

**Monochromatic microdiffraction probes highly textured/single crystal samples**

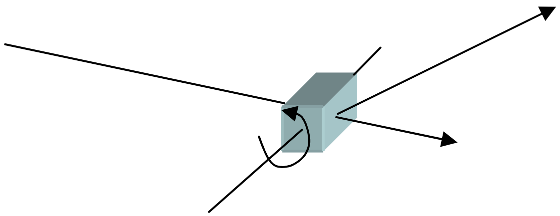
Fresnel Zone Plate



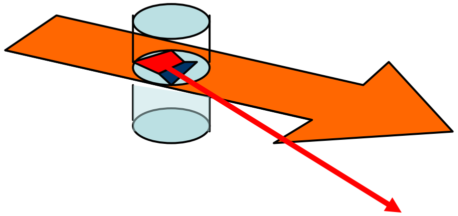


# At least four directions in Microdiffraction

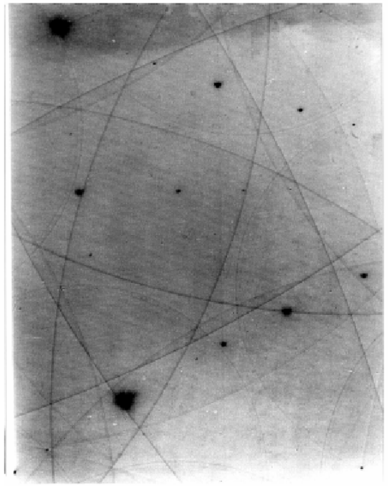
- Monochromatic crystallography
  - best S/N for simple crystals



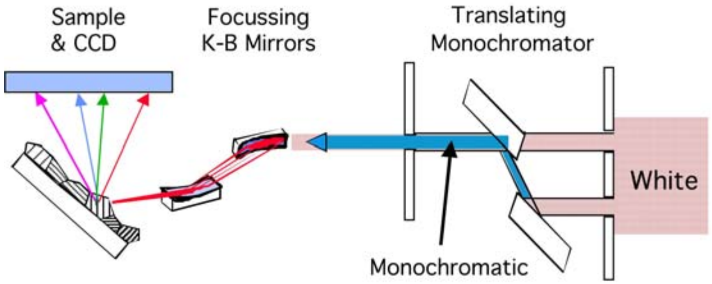
- RISØ/ESRF 3DXRD
  - best depth probe, fast



- Kossel Line
  - High angular resolution
  - Absolute strain

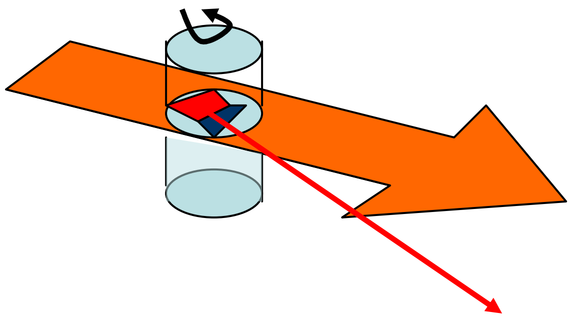


- Polychromatic microdiffraction 3DXRCM
  - Best spatial resolution
  - Deviatoric/absolute elastic+plastic strains

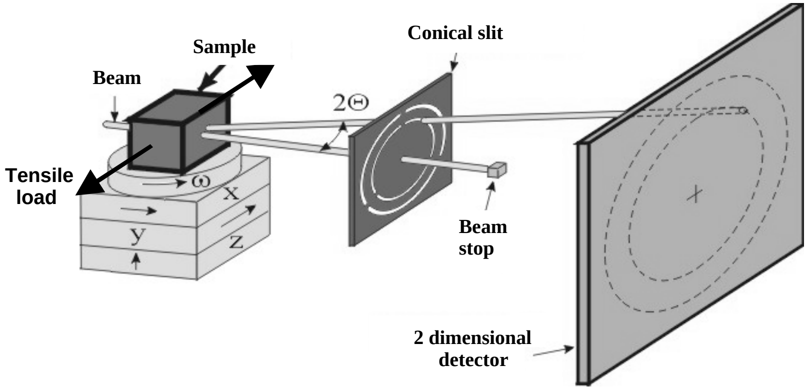


# 3DXRD Microscope emerging tool for studying mesoscale dynamics

- Singly focused monobeam illuminates numerous grains
  - Bragg condition satisfied by single rotation

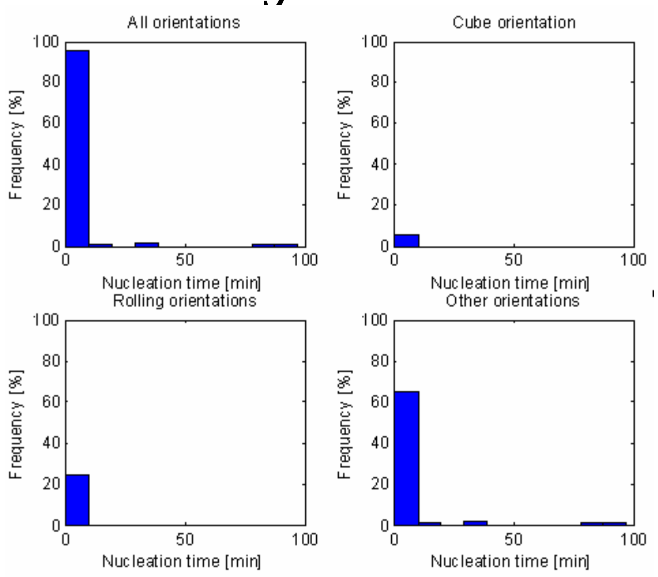


- Grain outline determined
  - Ray tracing
  - conical slit
  - Back-projection tomography
- E>50 keV allows deep measurements

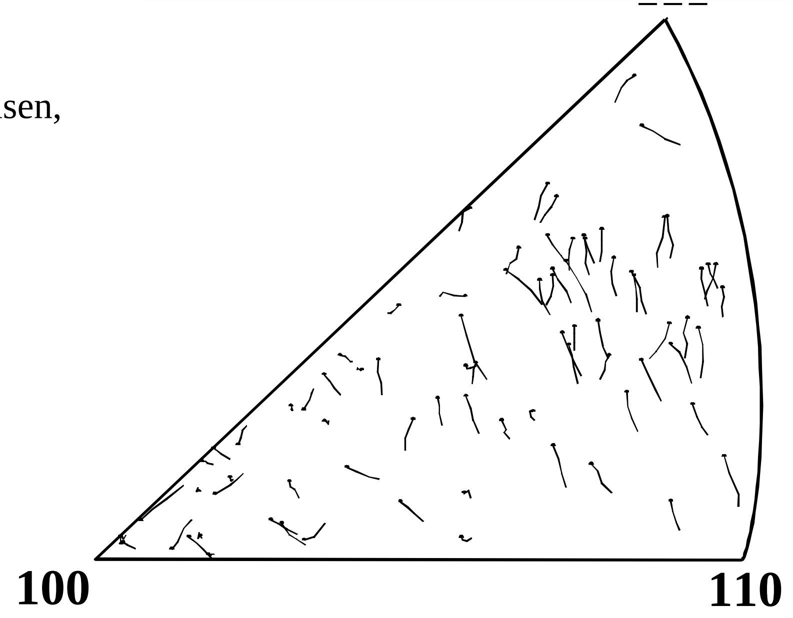


# 3DXRD Microscope powerful dynamics probe

- Recrystallization growth individual grains-deep
  - E. M. Lauridsen, D. Juul Jensen, U. Lienert and H.F. Poulsen (2000). *Scripta Mater.*, ***43***, *561-566*

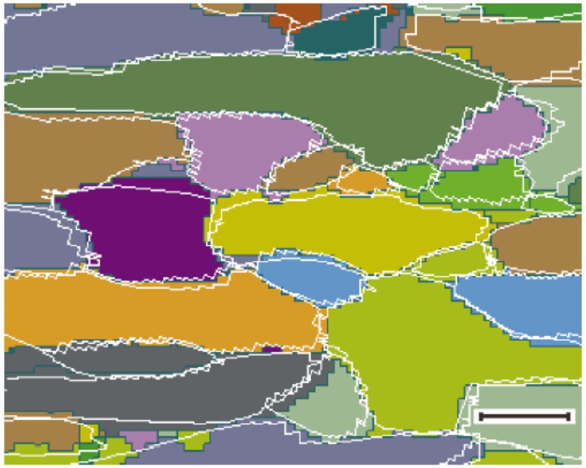



- Rotations/texture evolution individual grains during deformation
  - Tests deformation models
  - L. Margulies, G. Winther and H.F. Poulsen, Science **291**, 2392-2394 (2001).



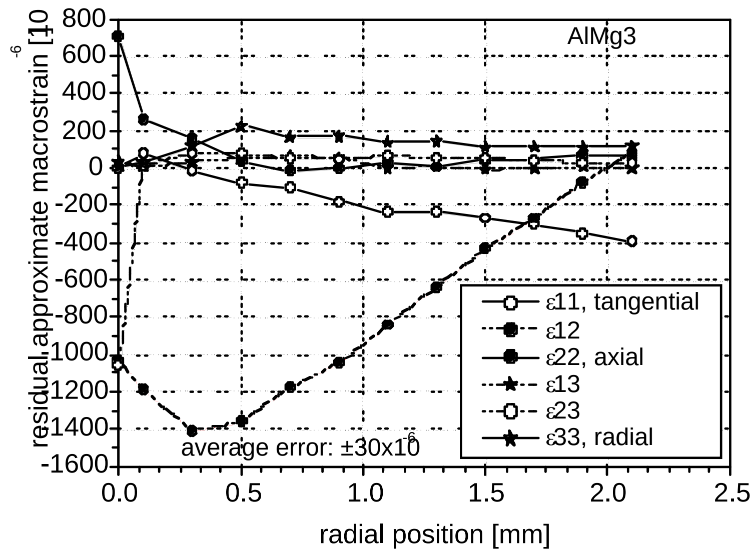
# 3DXRD Microscope provides additional powerful capabilities

- Grain boundary mapping in coarse grained materials-5μm
  - Poulsen et al. J. Appl. Cryst. 34 751-756 (2001)



- Single crystal refinement for polycrystals

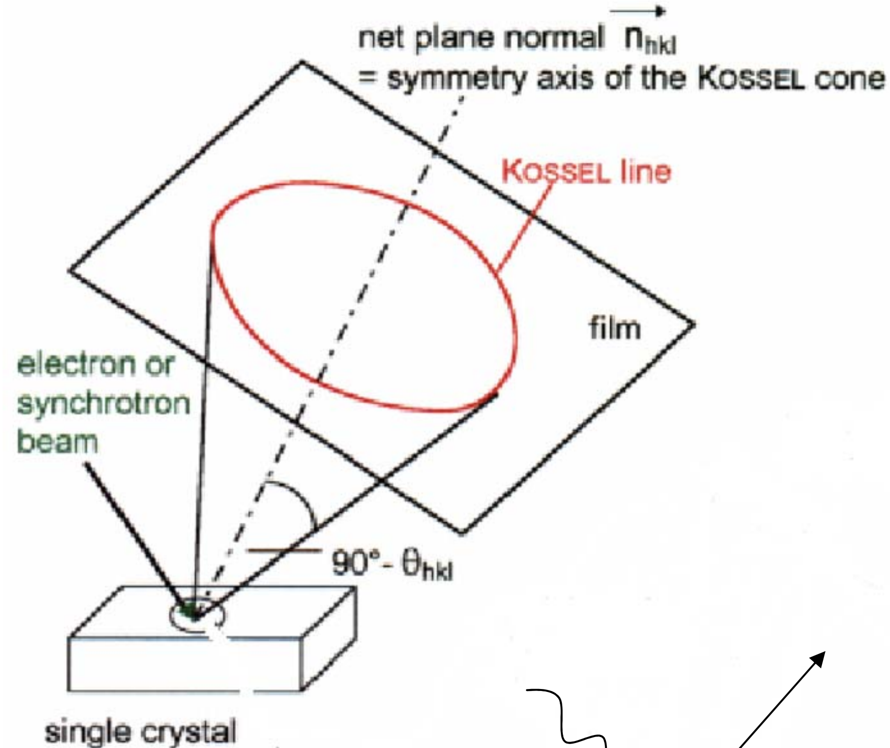
- Macro/microstrain



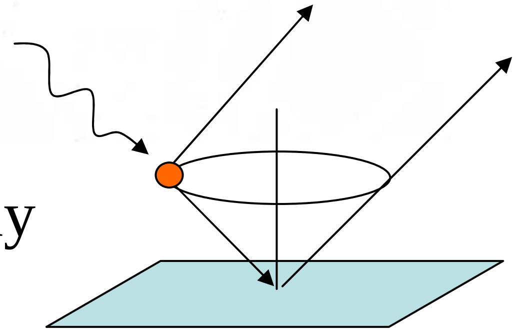

Strain tensor elements in torsion sample

# Kossel-line microdiffraction elegant technique - eliminates sample rotations

- Absolute lattice orientations and spacings
  - 0.01°
- Insensitive to grain orientation
- Poor signal-to-noise

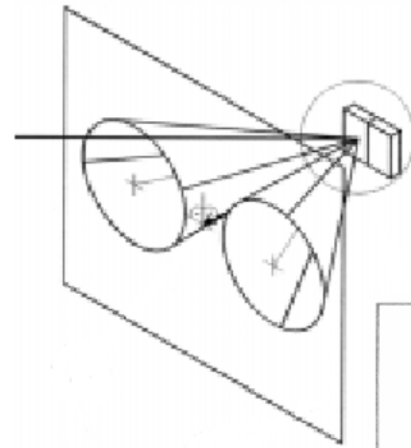


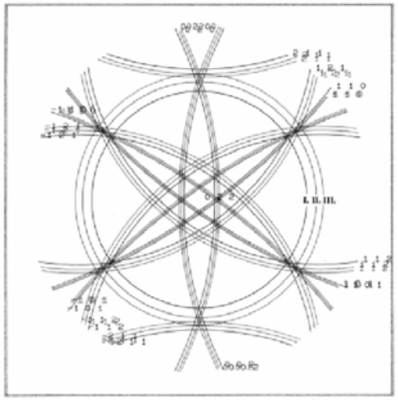

High resolution technique suited to few nearly perfect grains



# Kossel microdiffraction applied to materials

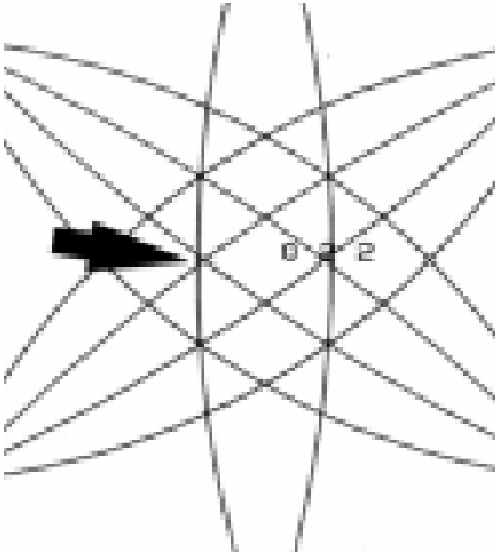
- Cu bicrystal misorientation
  - 0.15° -0.01 °





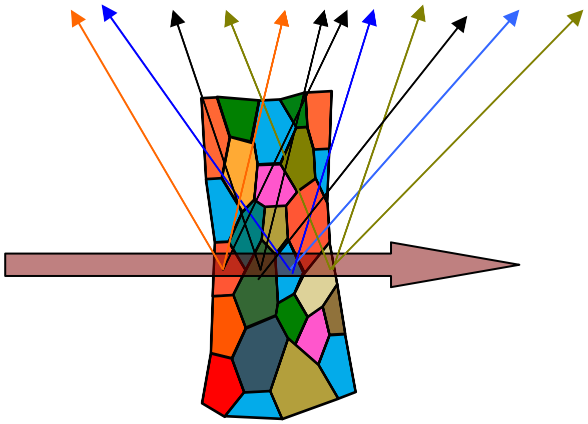
- Lattice constant in NiAl, $Fe_{1-x}Al_x$
  - $\Delta a/a < 3 \times 10^{-6}$

- Lattice distortions



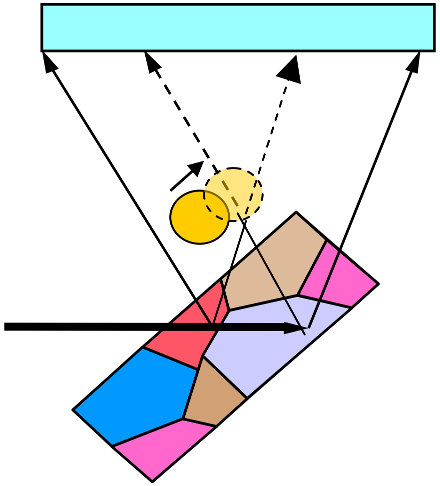
# Polychromatic microdiffraction well suited to intra- and inter-granular measurements

-Sample does not need to be rotated!



Laue patterns from subgrain volumes by differential aperture microscopy

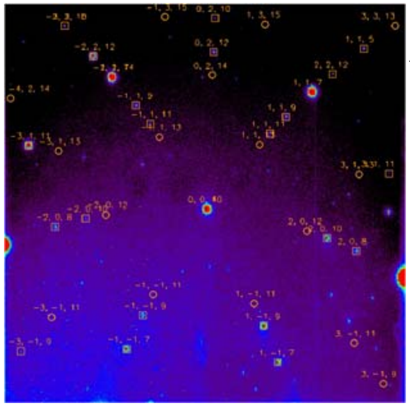
Sensitive to defects



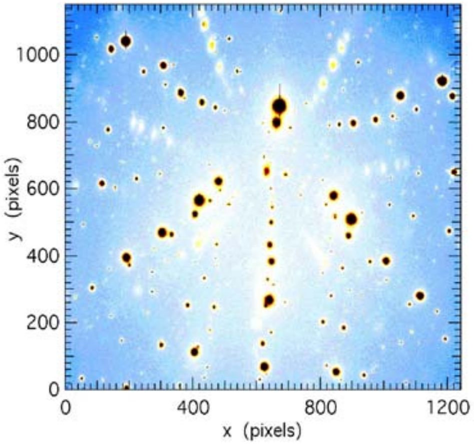
**Larson BC**, Yang W, Ice GE, Budai JD, Tischler JZ
**Nature** 415 (6874): 887-890 2002

**3D nondestructive probe of stress/strain/crystal structure!**

# 3D nondestructive probe correlates mesoscale structural heterogeneities and driving forces

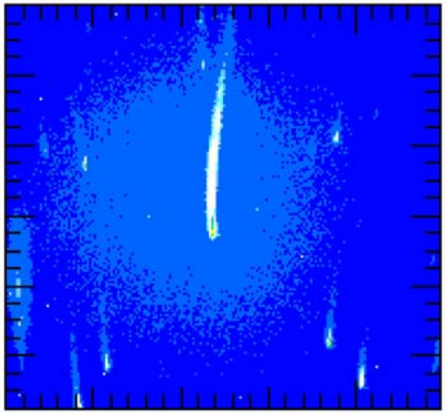


Phase/phase boundaries

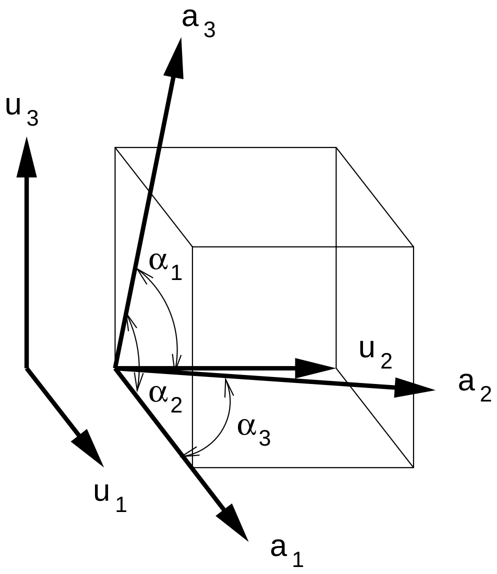



Texture (0.01º)/grain boundaries

Elastic strain ($1 \times 10^{-4}$)



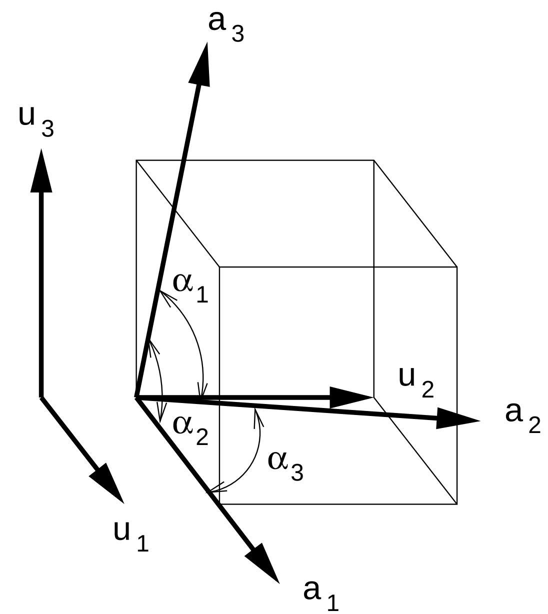
Deformation



# Strain is derived from unit cell parameters

$$A_{Meas} = TA_0$$

$$_{ij} = (T_{ij}+T_{ji})/2 - I_{ij}.$$

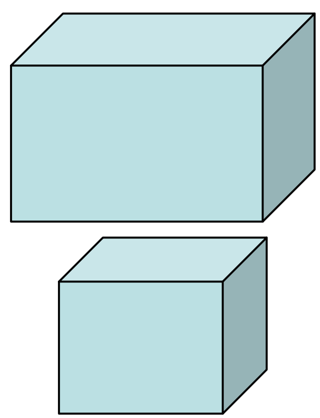



**Accurate measurements require absolute calibration**

**monochromator energy to ~1 eV**

**CCD to 0.2 pixels ~0.01 degrees**

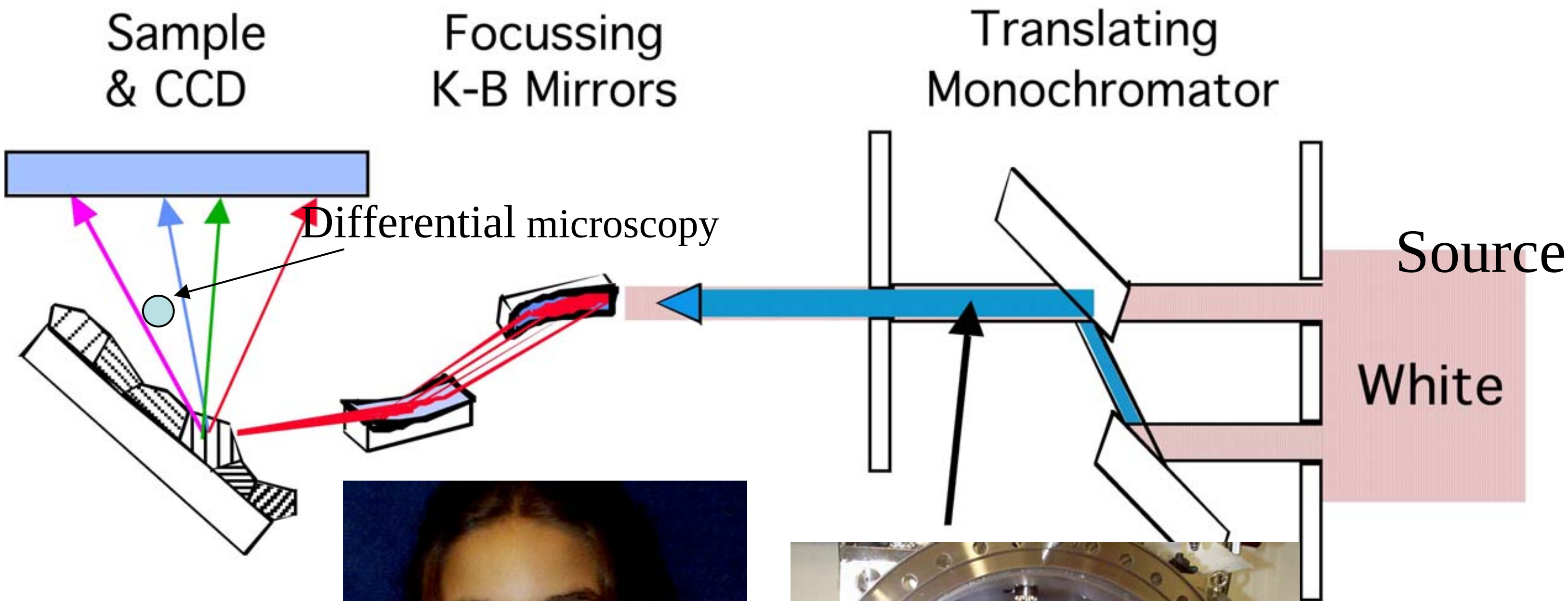
**Deviatorial strain tensor from single crystal Laue pattern**

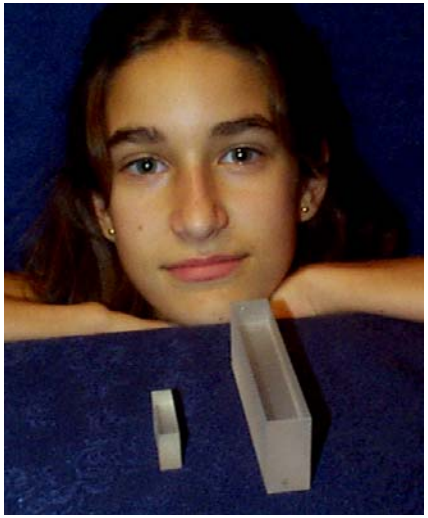


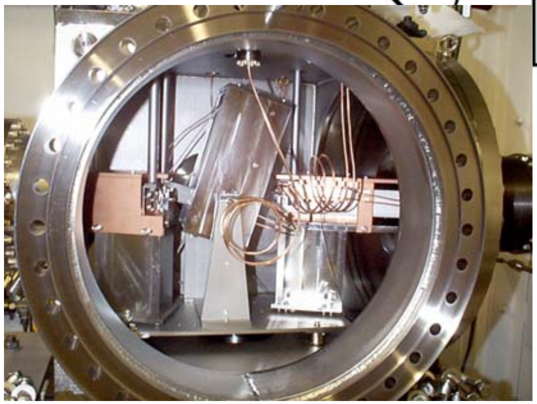
4 reflections $\Rightarrow$ deviatoric strain tensor

+ 1 energy $\Rightarrow$ full strain tensor

# 3-D X-ray Crystal Microscope has 5 key Elements

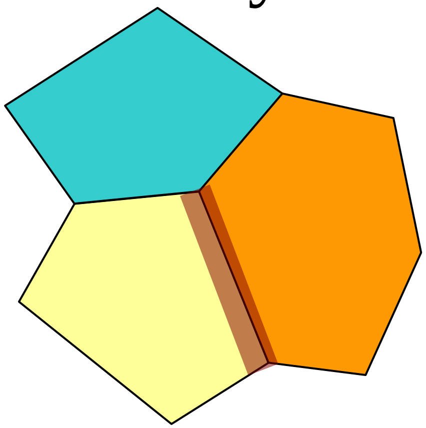


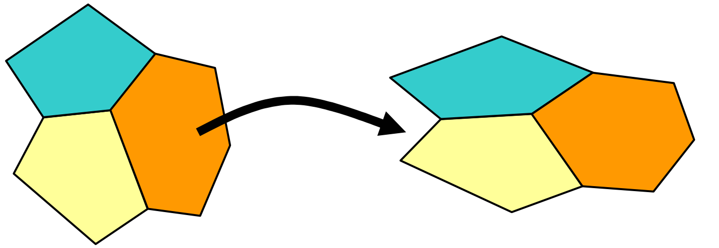


**$<0.3 \times 0.4 \times 0.7\ \mu m^3$**
**strain~$10^{-4}$-$10^{-5}$**

# How grain boundary/polycrystal networks interact - a central materials challenge 21st century

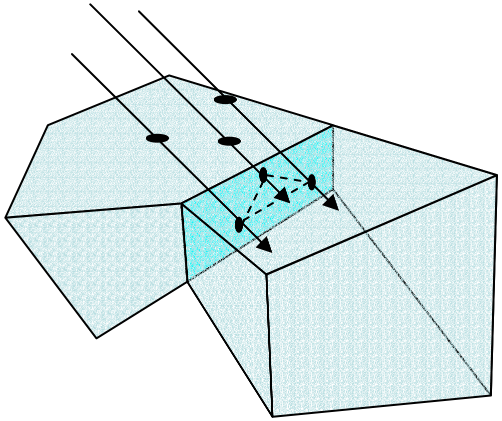


- What are the constitutive equations at grain boundaries?
  - How do they change with boundary type
- What are ideal microstructures?
  - How do different networks evolve during processing and in service?

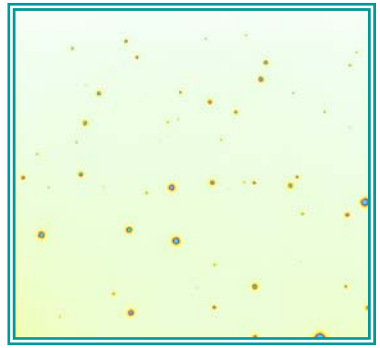


- How can grain boundary distributions be controlled?
  - Grain boundary engineering
- Nanophase and advanced layered materials

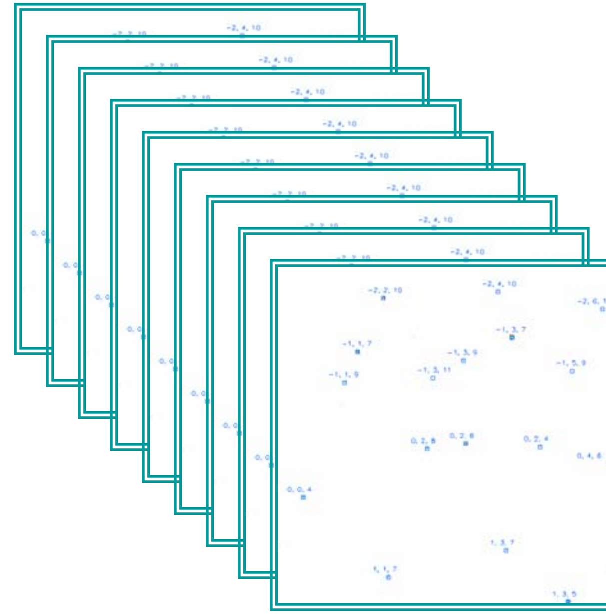
# 3-D Study of Grain Boundary Types



Assuming a locally planar grain boundary, three linearly independent intersects determine a grain boundary normal.



Depth Resolving



Indexing

**Orientation Matrix of Each Grain**

Finding Out Grain Boundary / X-ray Beam Intersects in 3-D

**Misorientation Angle & Rotation Axis**

**Angle Between Rotation Axis & Boundary Normal**

**Boundary Plane Normal**

CSL Theory

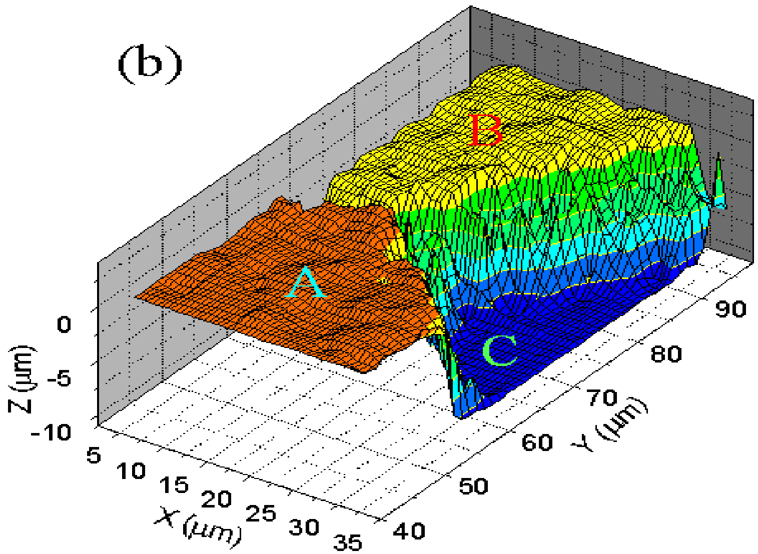
**Possible Σ Type**

**Twist (0°) or Tilt (90°) Type?**

# Unprecedented precision addresses long-standing issues

- Misorientations vs. Σ
  - Theoretical max misorientation increases as Σ *decreases*
  - Measured misorientations increase *with* Σ

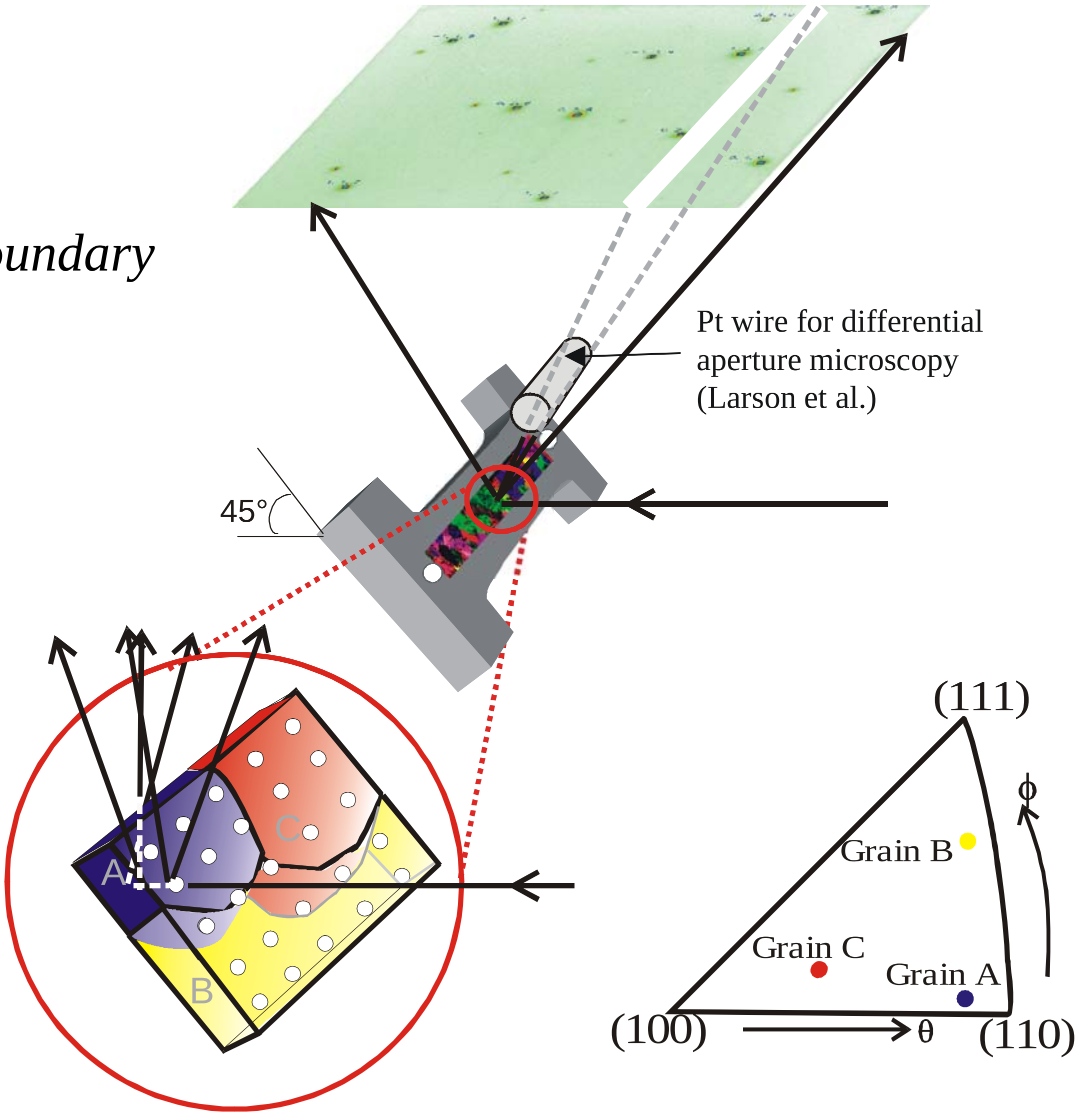
- Grain boundary normals
  - Ideal directions should have lower energy
  - Faceting may remove energy advantage



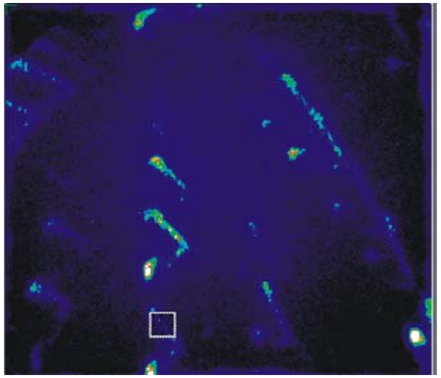

Morphology of Ni triple junction

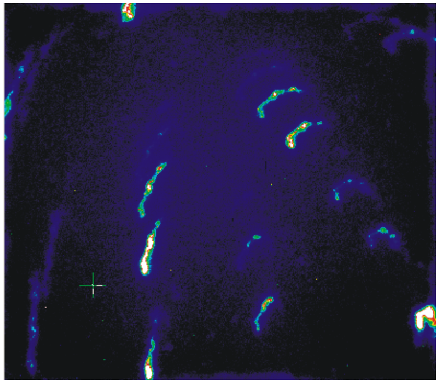
# Measurements of plastic deformation correlate behavior to structure

3D measurement of grain rotations/translations *with boundary conditions*

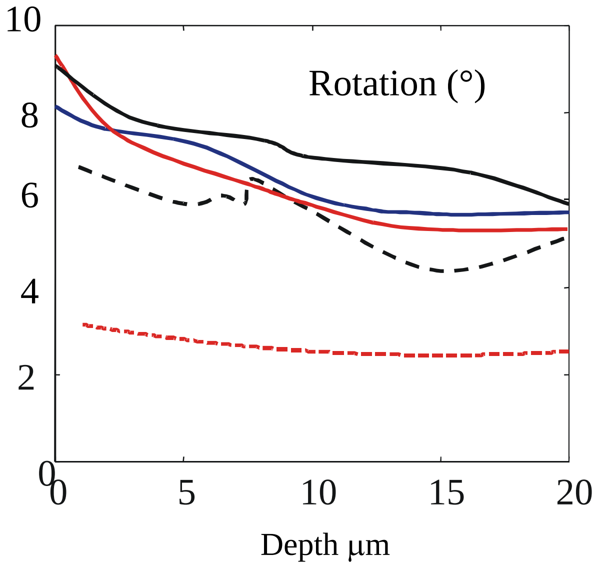


# Dramatic changes in dislocation network with depth

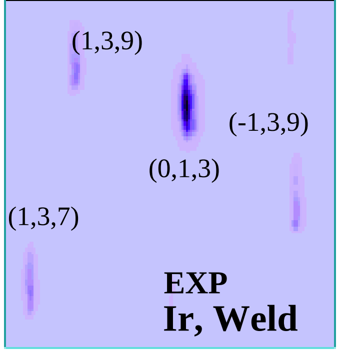




Consistently large rotations near free surface

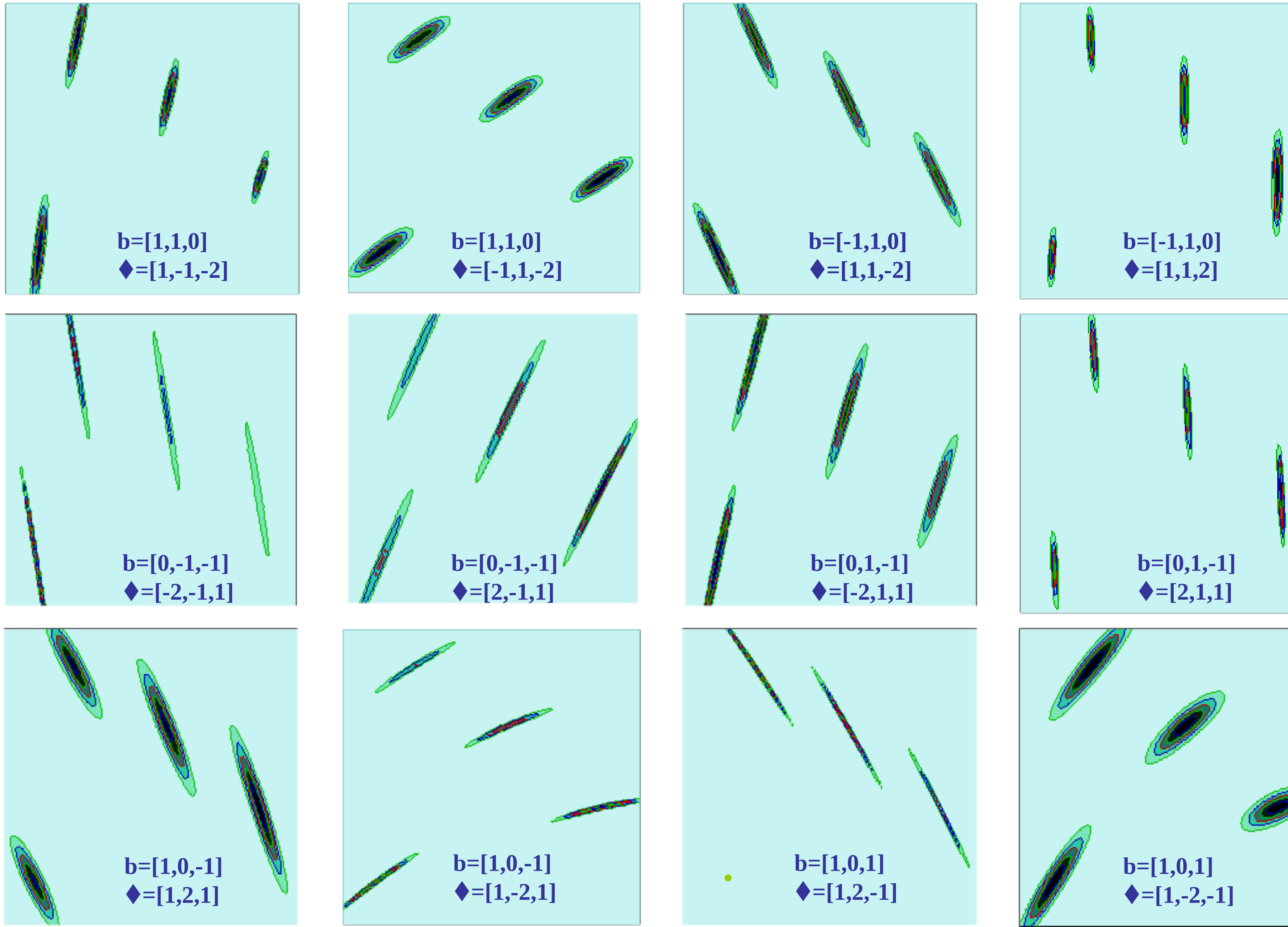


# How Do 12 Slip Systems Affect the Laue Pattern?




*Surface normal (013), $n^{+}=0.1n$, $L=500b$*

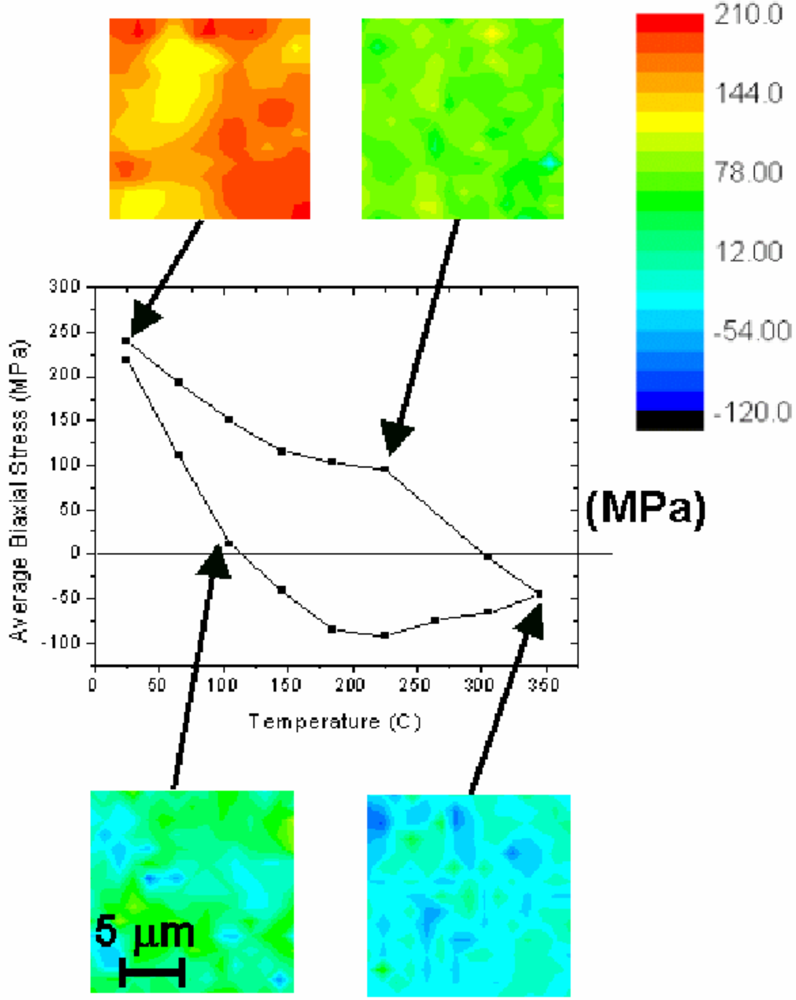
- *Slip System Changes the Direction of Streaking*
- *Contrast factor changes the length of the streak*
- *No Streaks for Some Reflections*



# Tamura et al. studied stress inhomogeneity in a thin Al (Cu) film as a function of T

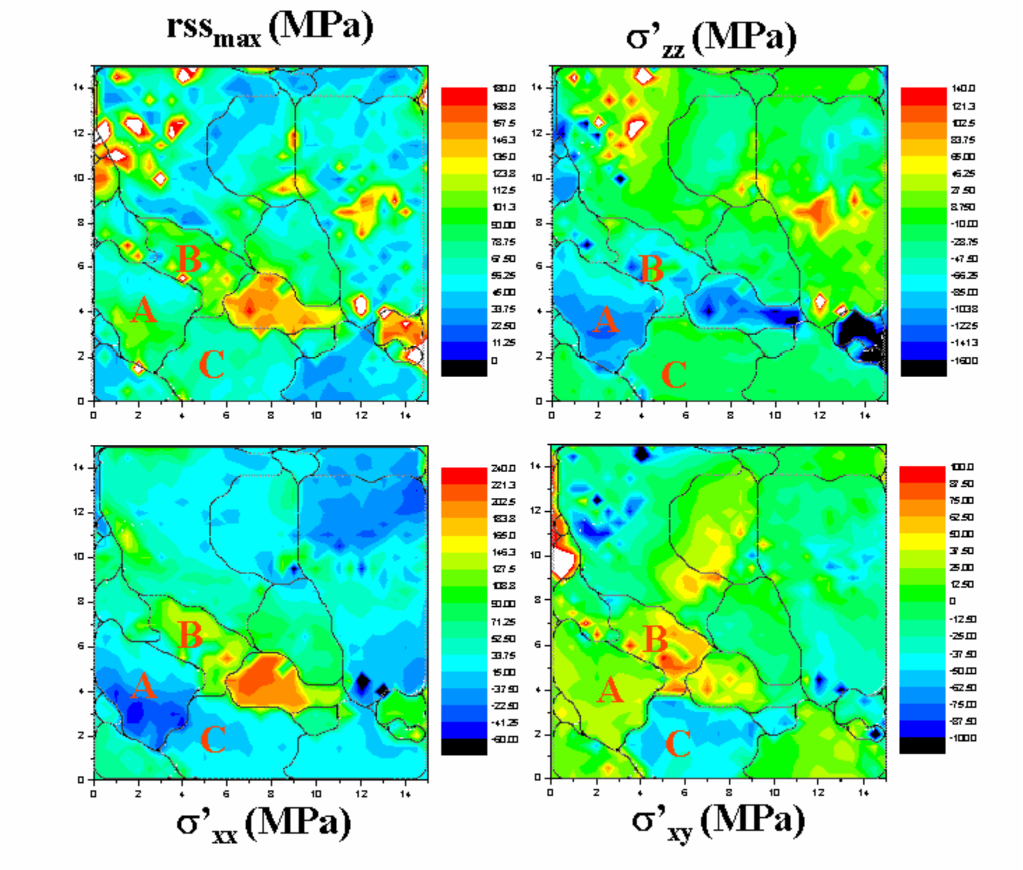
- Variations clearly observed to correspond to grain anisotropies

- Biaxial symmetry of system observed only on average.

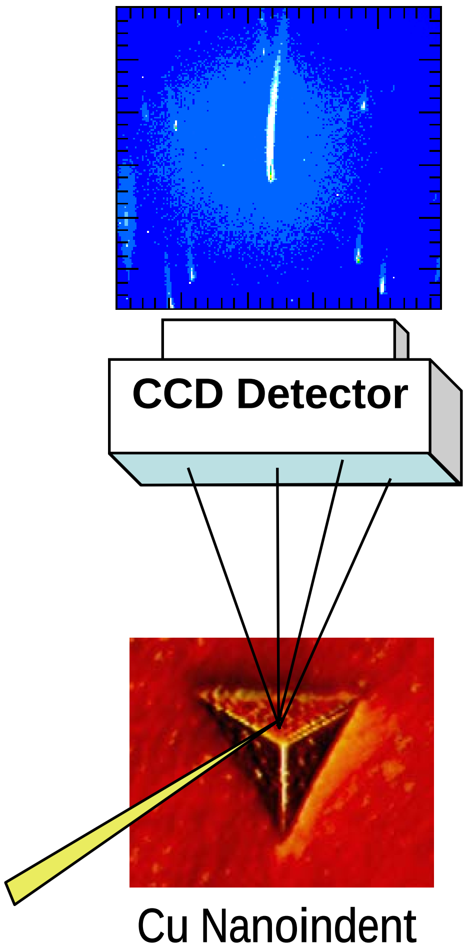


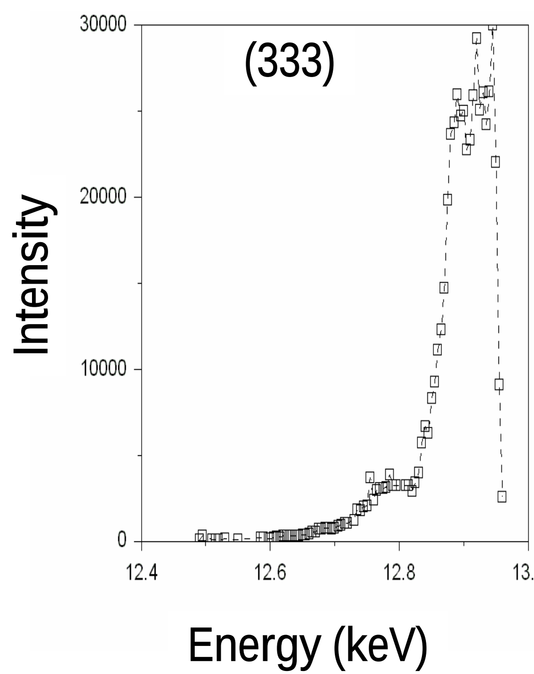
# Spolonek et al. Resolved shear stress observed in Cu films

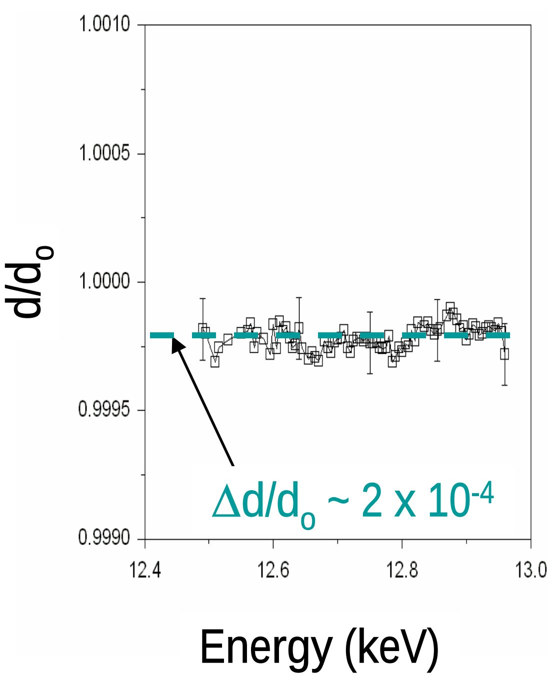
- Note that stress can be calculated from single crystal constants
- Stress varies with grain morphology and orientation



# Monochromator Energy Scan to Determine Residual Stress/Strain Below Nanoindent in Cu

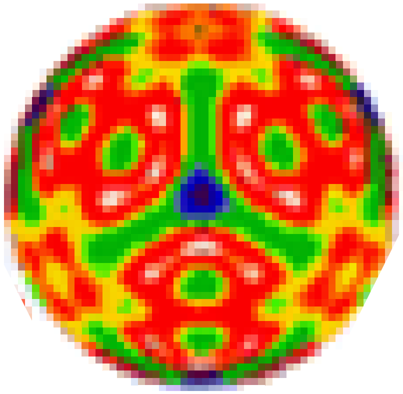


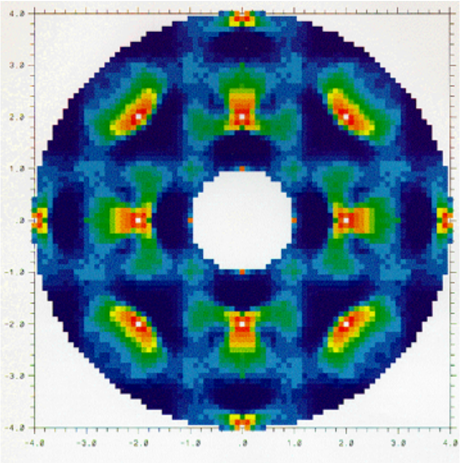
# Intense synchrotron sources will enable advances in understanding local structure of solid solution alloys

- High intensity + area detectors→
  - ***Time resolved***
  - ***Combinatorial***



**Holt, Wu, Hong, Zschack, Jemian, Tischler, Chen, Chiang, *Phys. Rev. Lett.* 83 3317 ( 1999).**

- Small- high flux beams with E resolution < lifetime broadened hole width→
  - ***Ultra precise pair correlations*** from anomalous scattering
    - Chemical order to many shells
    - Static displacements <0.001 nm

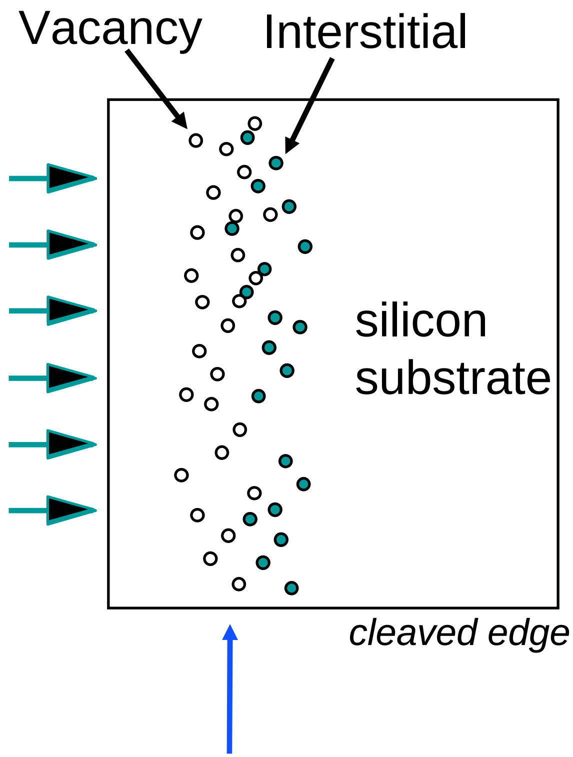


**Ice, Sparks, Habenschuss, Shaffer, *Phys. Rev. Lett.* 68 863 (1992).**

## What can we learn about local alloy structure?

# Micro-diffuse scattering applied to High Energy, Self-Ion Implantation in Si

**1-10 MeV $Si^+$**

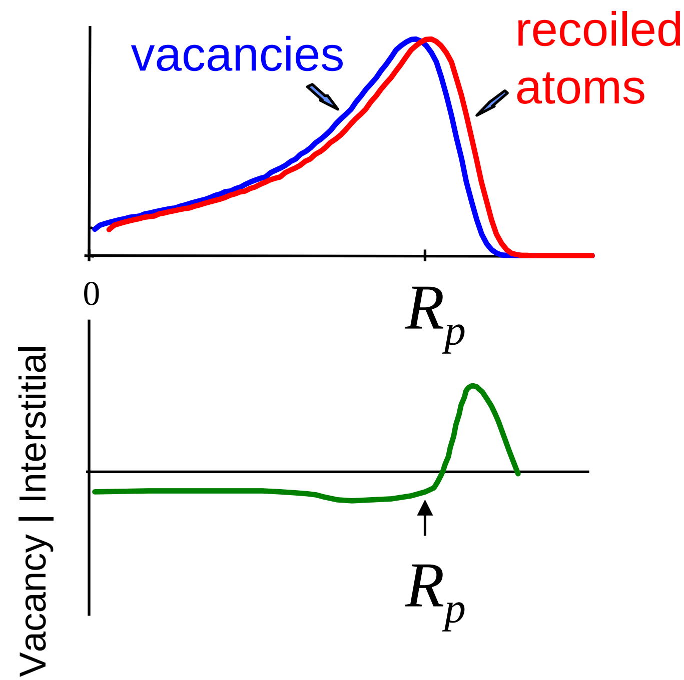


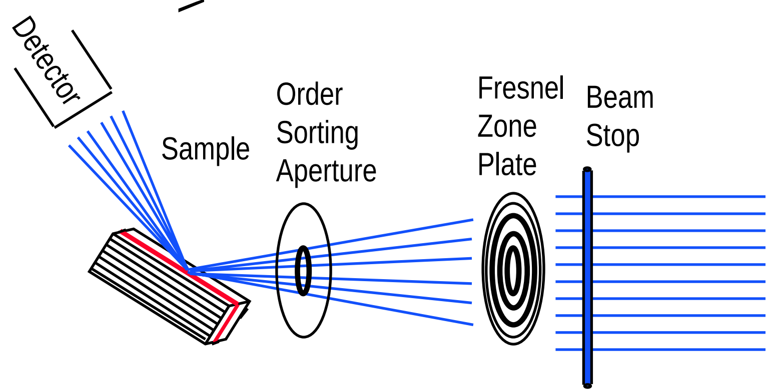

**X-ray Microbeam**

•cleave sample in cross-section

•translate to probe depth dependence

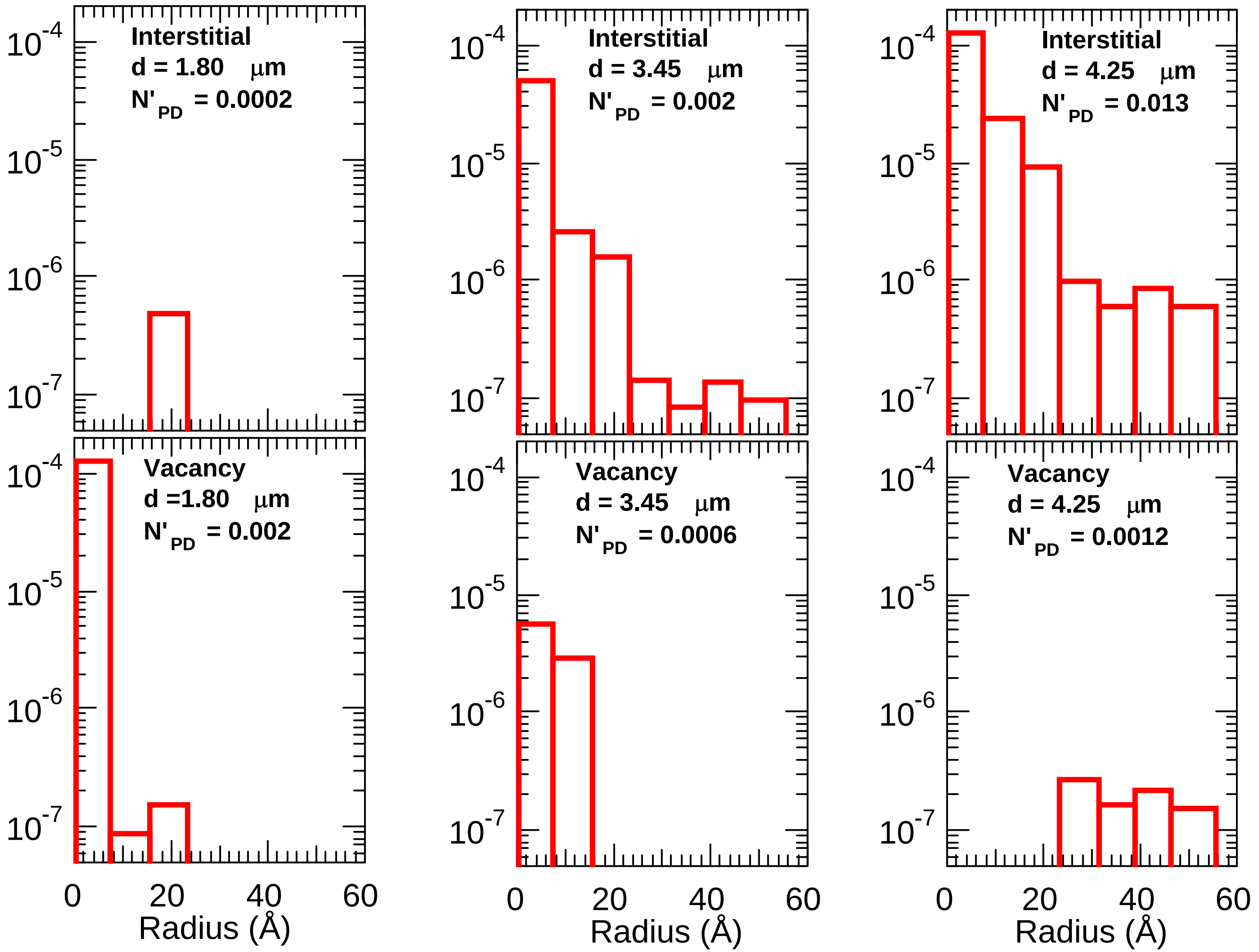
Spatial separation of recoils and vacancies due to momentum transfer



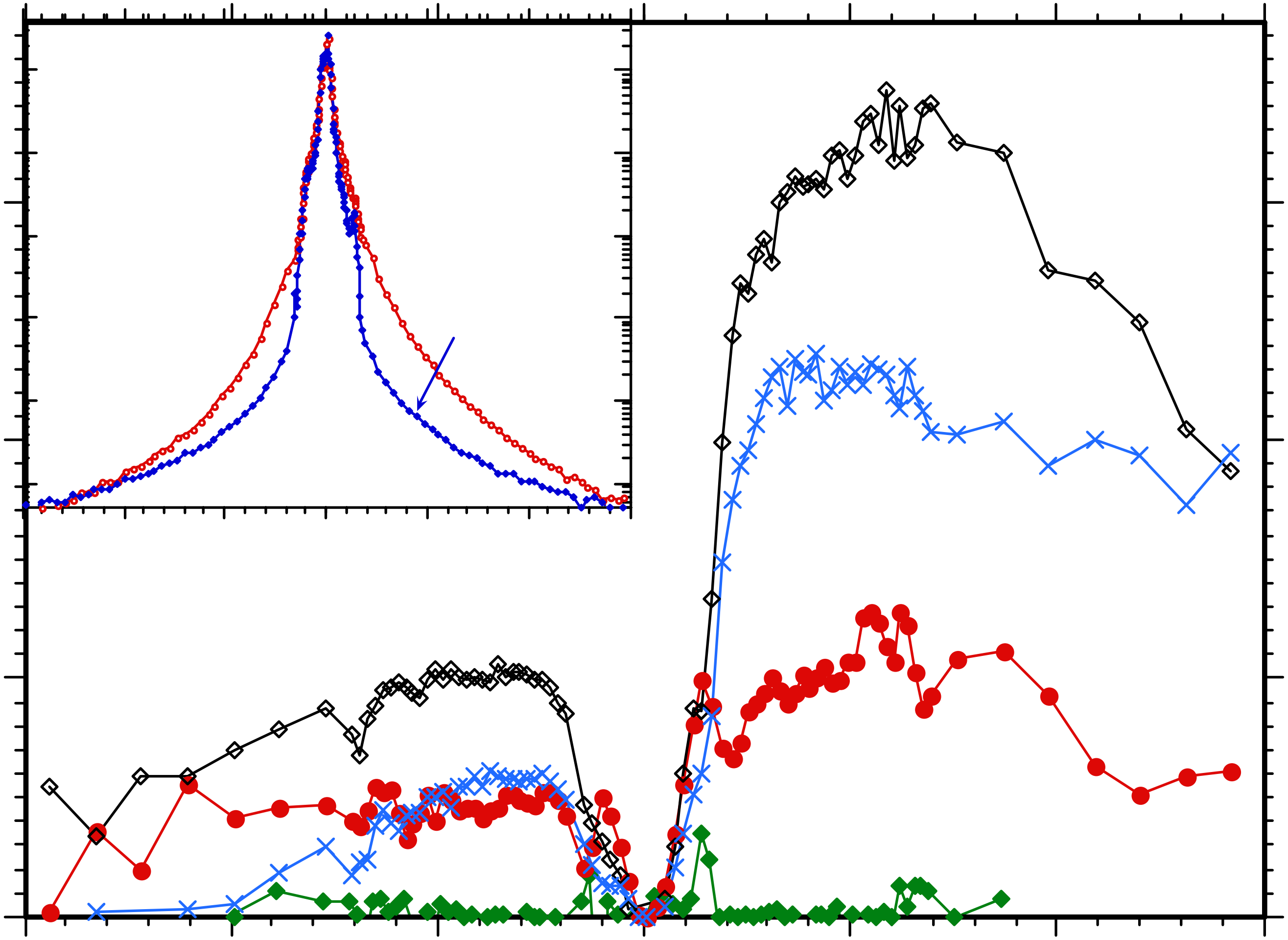

*Yoon, Larson, Tischler, Haynes*

# Depth Dependence of Size Distributions for Ion-Implantd Si



# X-ray Diffuse Scattering

Huang theory $\Rightarrow$ for $Q \ll 1/R$, $I \propto Kb\pi R^2/Q^4$



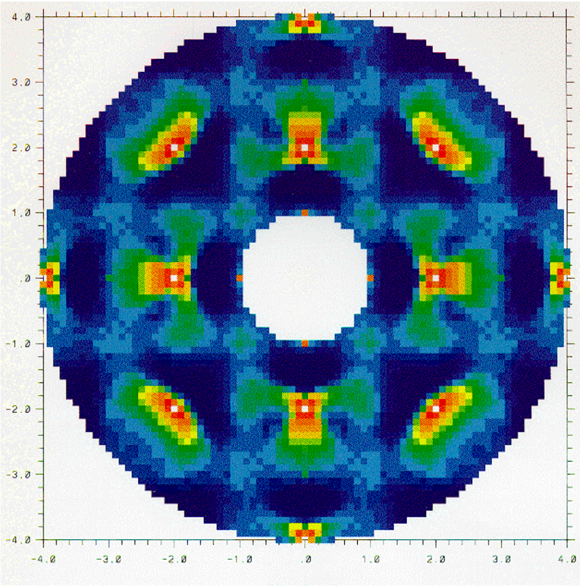
# Weak SRO can be probed with advanced microbeam

- Fe-Ni Alloy have weak atomic SRO-
  - Above ordering temperature difficult to measure in lab

- Anomalous scattering allows for measurements with synchrotron radiation
  - 2nd generation synchrotrons

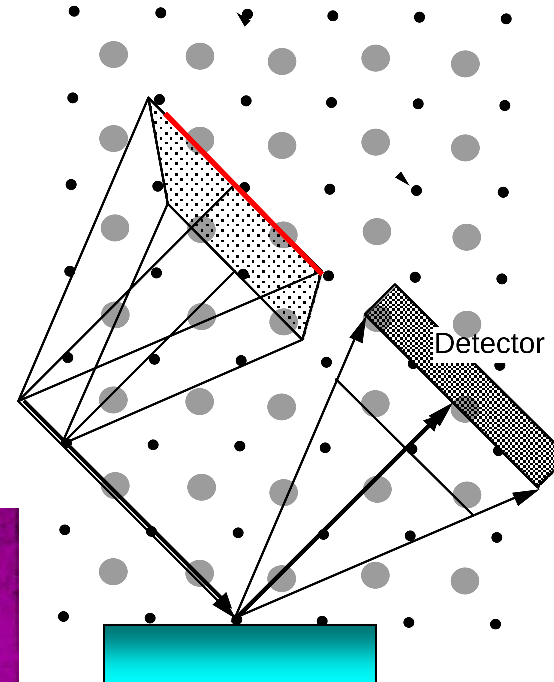
- Single crystal samples + Diffuse peak allows comparison of SRO heterogeneity with submicron resolution

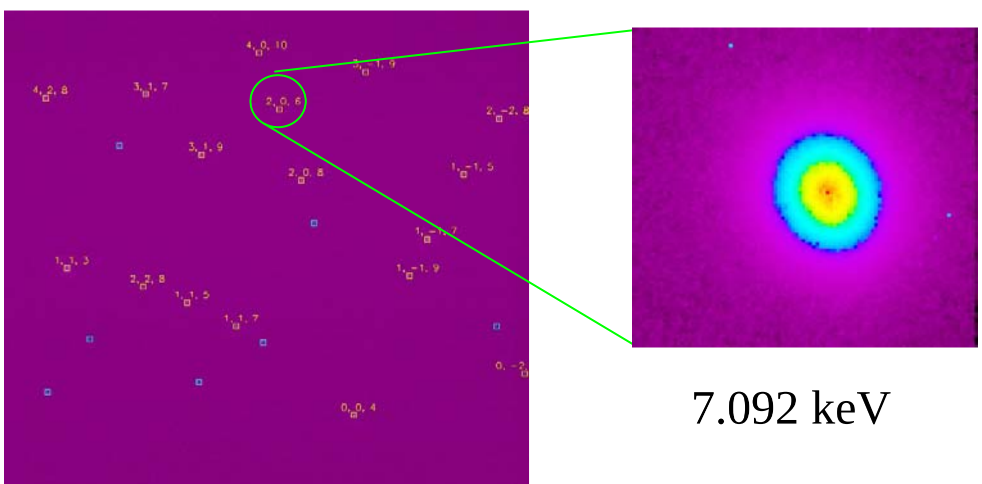
- Magnetic annealing modifies chemical SRO- order type; domain size?



# SRO heterogeneity in magnetically annealed single crystal can be studied by microbeam

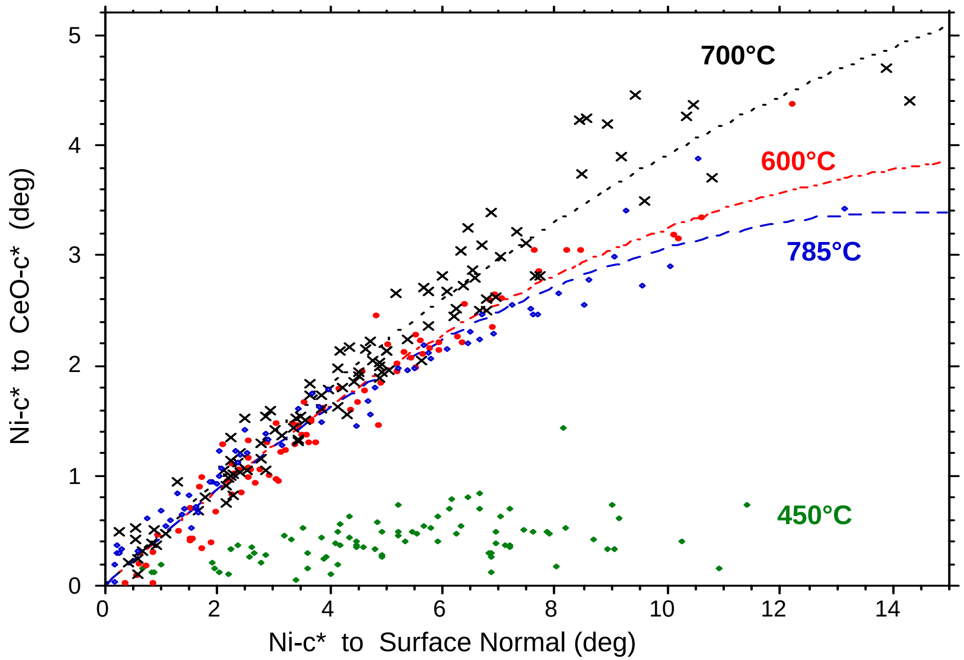
- Align sample so SRO peak will be in detector at anomalous edge
- Move monochromator into beam
- Cut through reciprocal space

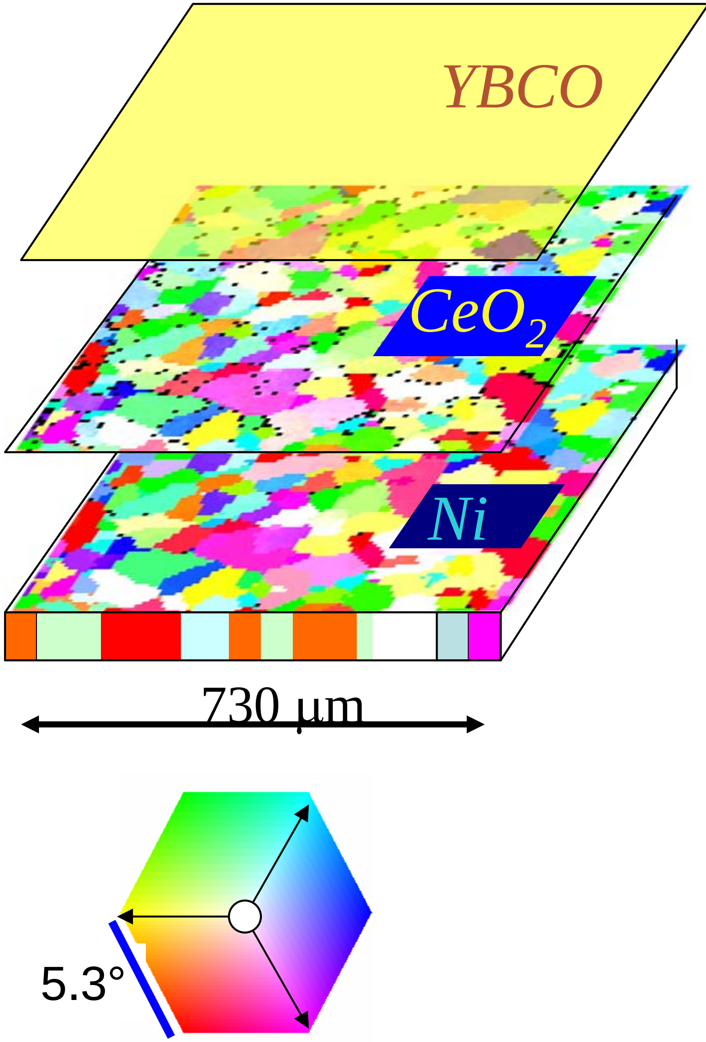


7.092 keV

# Microbeams enable combinatorial measurements on real samples

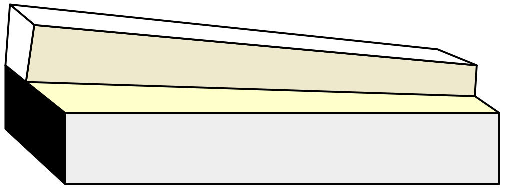


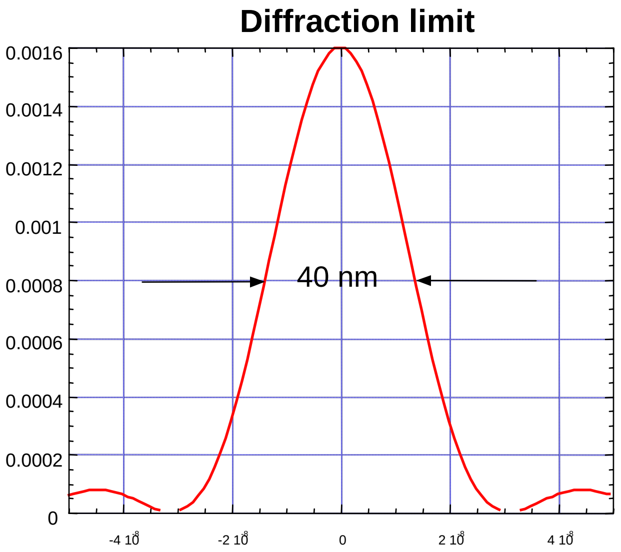

**Budai JD**, Yang WG, Tamura N, Chung JS, Tischler JZ, Larson BC, Ice GE, Park C, Norton DP **NATURE MATERIALS** 2 (7): 487-492 JUL 2003

# Hard X-ray 20-50 nm probe will revolutionize materials nano- science

- **EXAFS**
  - **Co-ordination+bond distances in nanoscale particles**

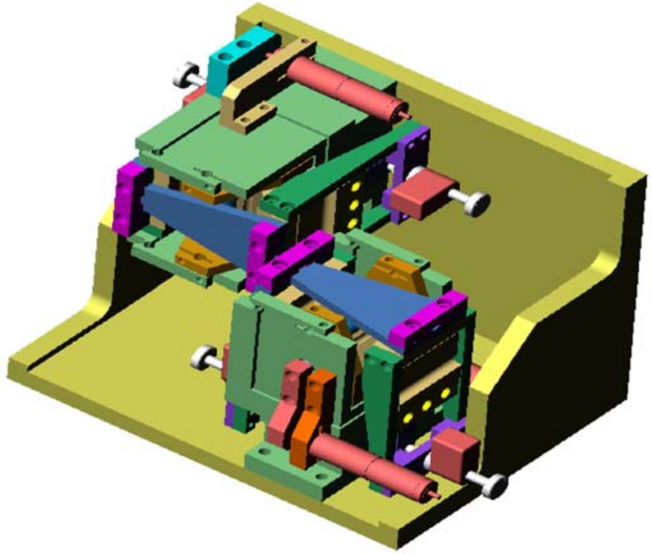


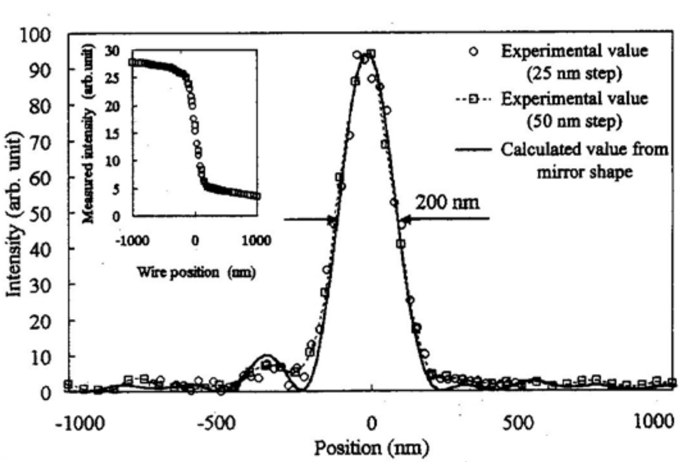
- **Coherent diffraction**
- **NEXAFS**
  - **Chemistry**
- **Laue nanodiffraction**



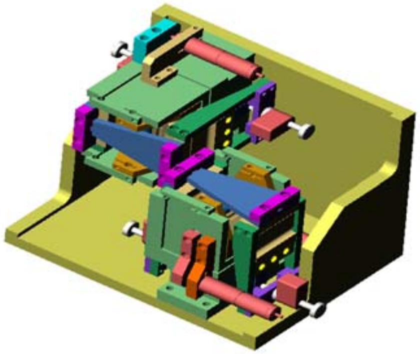
# ESRF/SPRING8 mirrors enter nanoscale range

- ESRF reported beams <90 nm using bent KB optics
  - Gain $10^6$
- Spring 8 reported <200 nm diffraction-limited focusing with polished KB optics
  - Long working distance





# Microbeam science will overwhelm skeptics with improved hardware/software



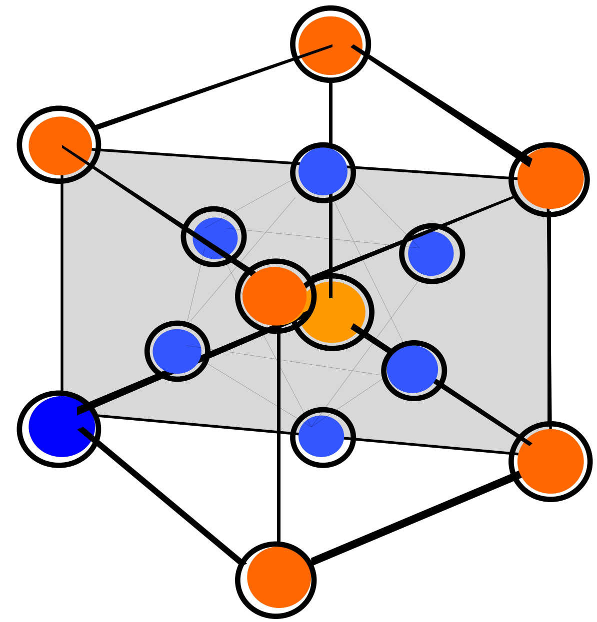
- Focusing to 20-50 nm
- Fast area detectors with
  - 16 bit readout in 1-10 msec
  - 10 eV energy resolution @ 10 keV
- Software for handing massive data and presenting it in comprehensible format

# Conclusion

- X-ray microprobes address long-standing challenges of materials science
  - Point-to-point property correlations within polycrystalline materials
  - Single-crystal characterization of individual grains/subgrains
- Smaller beams better detectors/optics will accelerate the ongoing revolution
  - Nanophase materials
  - Energy resolved area detection for fluorescence and polychromatic microbeam measurements.

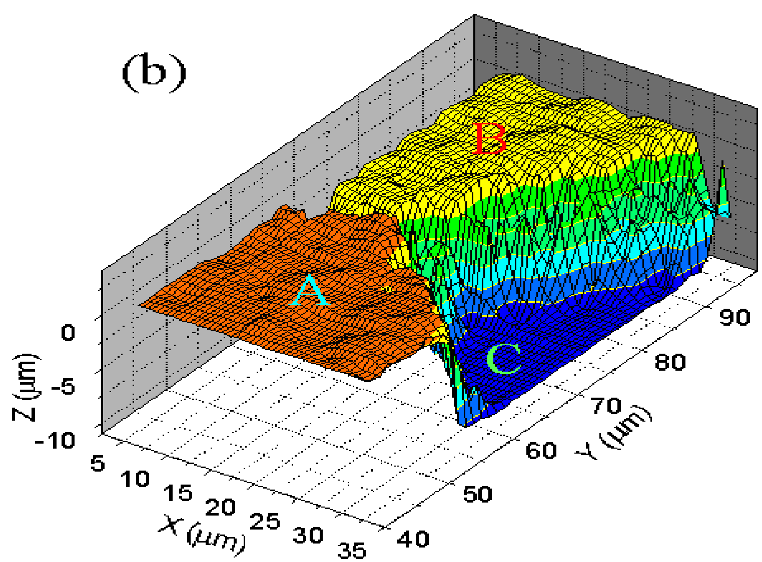
Come synchrotron colleagues who've gathered today
Let me tell you a secret –you know what I'll say
With small microbeams you now are freed
To study materials-on the scale that you need

*For microbeam science has planted the seeds*
*For materials characterization it answers our needs*
*What are the atoms –how are they spaced*
*And what are the defects –and where are they placed?*



Elemental concentrations- can now be seen
By intense fluorescence x-ray microbeams
3D without damage- chemistry/ bonding too
Opens materials opportunities – exciting and new

Small beams simplify - polycrystals its true
Resolving small regions where only a few
Grains interact -boundary conditions well known
Can models predict –how new grains are grown




What is the structure-we want to know
Is it crystalline, amorphous and how does it grow
How does it change from place-to-place
Resolved in real - and reciprocal space

What are the defects in grains micron sized
This new information would really be prized.
How do the defects distribute in space
With microbeam studies we'll put them in place.